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Fig. 1.

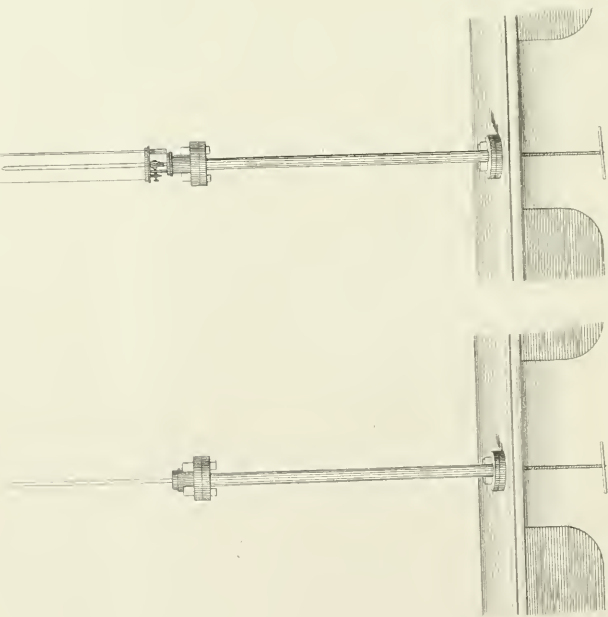


Fig. 2.

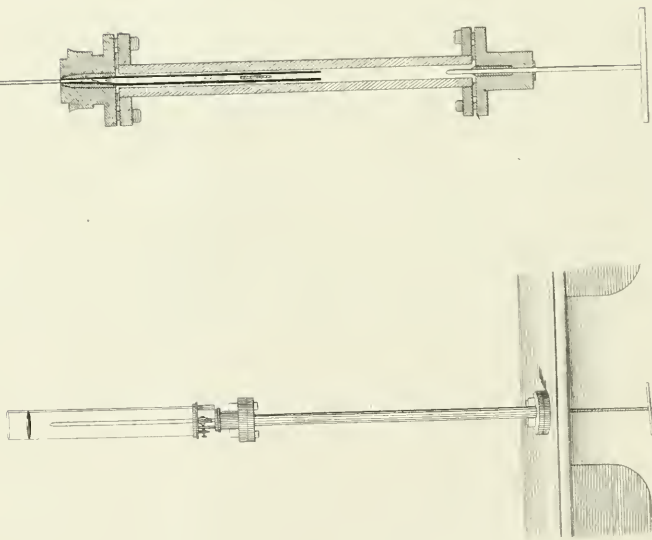


Fig. 3.

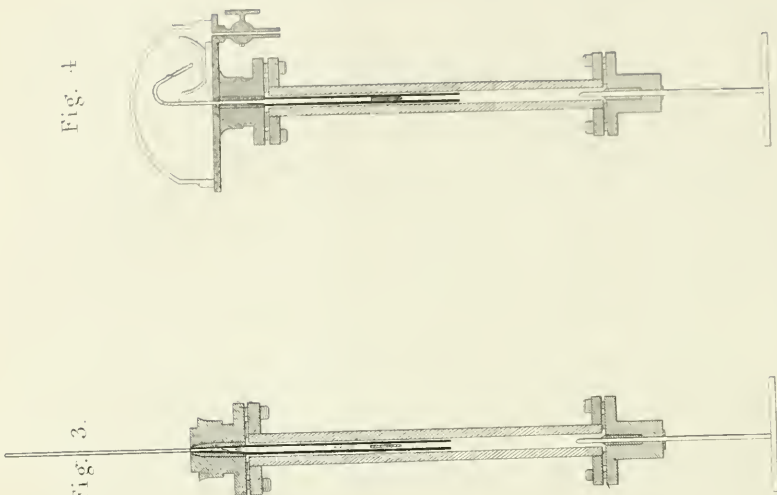


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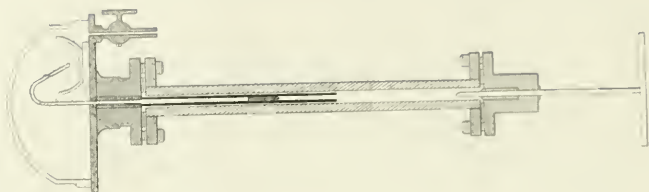
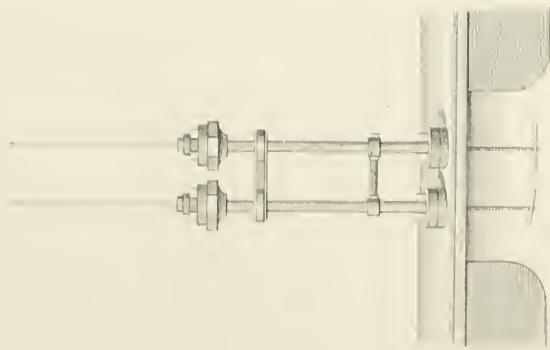
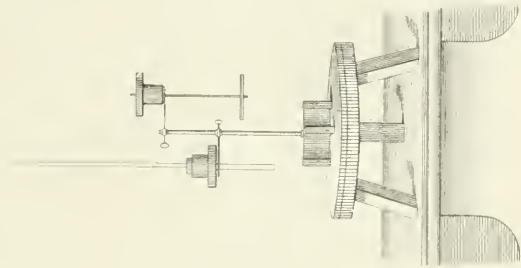


Fig. 5.



Wm. & C. C. C. C.

Fig. 7.



Wm. & C. C. C. C.

Anniversary Meeting, March 30th, 1869.

Mr. Warren De La Rue, President, in the Chair.

The following Report was read by the President:—

The President and Council have again to congratulate the Fellows on the continued prosperity of the Chemical Society, and to call attention to the fact that, notwithstanding the loss of seventeen Members from various causes, there is an increase in their number, as will be seen from the following statement:—

Number of Fellows (Anniversary), March 31st, 1868..	510
Since elected and paid admission fees	29
			<hr/> 539
Removed on account of arrears	5
Withdrawn..	8
Deceased	4
			<hr/> 17
Number of Fellows, March 30th, 1869	522
Number of Foreign Members (Anniversary), March 30th, 1868	39
Deceased (M. Schönbein)	1
			<hr/> 38
Present Number of Foreign Members	38
Associates	2

Fellows deceased:—

C. H. Berger, Esq., John Graham, Esq., Dr. W. B. Hera-
path, F.R.S., Robert Porrett, Esq., F.R.S.

Fellows withdrawn:—

Rev. John Barlow, G. W. Brown, Esq., Samuel Crawley,
Esq., T. M. Evans, Esq., Rev. B. W. Gibsons, Lieutenant
H. M. Hozier, J. H. Richardson, Esq., Robert Barton,
Esq.

From the statement of the Treasurer, it appears that the
income is in excess of the expenditure by the amount of
£279 5s. 6d.

Although it would be perfectly impracticable to give even the most condensed account of the progress of chemistry within the limits of this report, nevertheless it may be useful to recall to recollection a few noteworthy additions made to our science since I had the honour of addressing you at our last anniversary.

Professor Graham, in continuing his researches on Occlusion, has arrived at results which strongly support the hypothesis of the metallic nature of condensed hydrogen. Metallic palladium, which exhibits in a most remarkable degree the property of occluding hydrogen, has been found to exhibit, when charged with this gas, changes which can scarcely be otherwise interpreted than by assuming that hydrogen combines with the palladium, forming in all probability a true alloy. The increase of bulk and the consequent reduction of specific gravity, the augmentation of the magnetism, the conservation in a high, though diminished degree, of the tenacity and electric conductivity, all point to the existence of *hydrogenium* as a metal.

The application of that branch of physico-chemical research, spectrum analysis, to astronomical investigation has, during the past year, contributed greatly to our knowledge of the constitution of the sun's atmosphere. It has been shown by the accordant results of the several expeditions organized to observe the total eclipse of August, 1868, that the luminous prominences, which frequently extend to a distance equal to one-tenth of the sun's diameter beyond his limb, consist of incandescent gases, the chief of them being hydrogen in a variable but high state of tenuity. On the other hand it has been proved by the polariscope that the corona is a portion of the atmosphere not self-luminous, and that it shines by light reflected from the photosphere. M. Janssen and Mr. Lockyer have rendered the existence of the prominences evident by means of the spectroscope at times when the sun is not eclipsed; and quite recently, both Mr. Huggins and Mr. Lockyer have been able, independently, to render the outlines of these appendages and the changes continually taking place in their forms distinctly visible whenever the sun can be observed under favourable atmospheric conditions.

Recent experiments by Mr. Sorby in this same branch of chemistry, spectrum analysis, promise to introduce a new field of research. In examining the absorption-bands of borax beads, in which various minerals have been dissolved and allowed to

crystallize, the presence of certain elements has been distinctly recognized. On applying this mode of investigation to several transparent minerals, more especially to the varieties of Zircon, he has observed a recurrence of absorption-bands, and the phenomenon is so characteristic that he is inclined to ascribe it to the existence of a new element. These peculiar bands are only to be seen in certain rare specimens of the Ceylon hyacinth or jargon, and not in the zircons of the northern localities (Norway, Siberia). In the latter Svanberg, nearly twenty years ago, supposed the existence of a new element, which he called Norium, and some observations made by Church on certain zircons, led him to infer that, besides zirconium, another new element was contained in them. It has still to be settled whether the jargonium, the norium, and the new element of Church are identical.

In another branch of physico-chemical research, the investigation of Landolt, on the Vapour-tensions of Homologous Compounds, has established the fact that the law of Dalton holds good within certain limits in bodies pertaining to the formic acid series.

Among the vast accumulation of facts bearing upon isomerism, must be noticed a very considerable number of new formations of organic compounds by synthesis. While the revelations of isomerism directly tend to increase the number of individual compounds, on the other hand the light thrown upon the chemical structure of compounds by the study of isomerism appears to be most instrumental in the promotion of synthetic chemistry.

As one of the most remarkable achievements in this direction may be cited the synthesis of alizarin, effected quite recently by Graebe and Liebermann. By a most exhaustive investigation of the quinone group, Graebe arrived at certain conclusions which led him to consider alizarin to be dioxyanthraquinone; and subsequent experiments have proved this supposition to be correct. It will be recollected that Limpricht had already, by a synthetical process, obtained anthracene from toluol, and that toluol, in its turn, has been obtained from benzol, benzol itself being a condensation-product from acetylene, and the latter resulting from the direct union of carbon and hydrogen. Synthesis has, therefore, built up a molecule containing as many as fourteen carbon atoms and ten hydrogen atoms. Anthracene

being a constituent of coal tar, this discovery will, in all probability, prove to be of considerable industrial value, by adding to the already numerous list of coal-tar colours, the most important of the colour-giving principles of madder.

Berthelot, by passing acetylene, olefiant gas, or marsh-gas through a red-hot tube, has found that certain condensation-products are produced, amongst which he identified benzol, styrolene, and naphthalene; benzol in particular being produced from acetylene in very considerable proportion.

I must not leave unnoticed the remarkable researches of Baeyer, on Mellitic Acid, and those of Hofmann, on the Compounds isomeric with the Sulphocyanic Ethers.

The parallelism existing between oxygen and sulphur compounds has received an additional link by the discovery of the true sulphur-urea by Professor Reynolds.

In technical chemistry, Miller's method of refining gold by means of a current of chlorine passed into the fused metal, deserves notice as likely to prove of importance in those distant localities where the economy of acids is essential.

Another very important and interesting process in practical chemistry, is the production of chlorine by passing the vapour hydrochloric acid, mixed with air, through clay-pipes, moderately heated in a furnace.

I have great pleasure in announcing that the new Catalogue of our Library has been printed, and is ready for issue; it will be sent to the Fellows as speedily as possible.

I must not pass over without notice an important event in chemical literature. I allude to the completion during the past year, of that classical encyclopædia, "Watts's Chemical Dictionary." This great work, while it faithfully represents the most advanced theoretical views, at the same time connects the nomenclature of the past and that of the present, with the greatest perspicuity. It cannot fail to prove of great value to the theoretical and the practical chemist; and I feel confidence in saying that it reflects credit alike on the author and his distinguished collaborators.

I now propose to give a brief notice of those deceased Fellows whose loss we have to deplore.

Mr. Capel H. Berger was born on the 6th November, 1839; he was connected with the well known firm of Lewis Berger

and Sons, of London, whose high reputation as makers of carmine and other pigments has been sustained for nearly a century. He took an active part in promoting the adoption, in England, of the French metrical system, and was, at the time of his decease, the treasurer of the International Decimal Association. To quote from a letter of the secretary, "he was much loved and appreciated by every member of the council of that body." His promising career was cut short by an accident. He died on the 21st June, 1868, from asphyxia, caused by the incautious use of carbolic acid for the relief of toothache.

Mr. John Graham, one of the original members of the Chemical Society, died in office, as Superintendent of the Coining Department of the Royal Mint, in February last. He was a younger son of the late James Graham, Esq., of Ballewan, Stirlingshire, and was born in 1812. After serving his time as an articled clerk to Mr. Ker, accountant in Glasgow, he applied himself to the study of chemistry, under the guidance of his brother, Professor Graham, then connected with Anderson's University. His fellow-students, Mr. James Young, and Mr. John Thom, have since risen to eminence in applied chemistry. On the recommendation of the late Charles Macintosh, F.R.S., Mr. John Graham early obtained an appointment as chemist in the well-known print works of Thomas Hoyle and Sons, Mayfield, Manchester, in which he afterwards became a partner. Dr. Dalton was on intimate terms with the members of this house, dining regularly every Sunday, during the greater part of his life, with Alderman William Nield, the head of the establishment. Later in life, Mr. John Graham erected new print works, in conjunction with Mr. John Kennedy, at Heywood, near Stalybridge.

Mr. J. Graham enjoyed the friendship of the late Walter Crum, James Thomson, of Primrose, Clitheroe, and Mr. John Mercer, and, in common with these gentlemen, did good service in the application of chemistry to calico-printing.

The practice of bleaching was also much improved in his hands. With reference to the bleach-works of Messrs. Hoyle, which were situated at Duckinfield, within a few miles of Ashton, he used to relate a curious incident:—On visiting the works one day, he found everything at rest. The foreman stated, in explanation, that by long experience he was satisfied

that they could not bleach when the wind was in the north-east, and that it was needless to try it, for the goods were infallibly covered with white spots when they came afterwards to be dyed. This was true, and on inquiry, the mischief was traced to small crystals of sulphide of iron, which were carried by the wind in question from the chimneys of certain distant works in which a highly pyritous coal was burnt.

Mr. John Graham conducted a series of elaborate experiments on the relative evaporating power and economy of boilers of different forms, upon which he communicated a paper to the "Manchester Memoirs" (vol. 15, p. 8, series 2). This inquiry is referred to with approbation by Mr. Hirn, of Colmar, in his valuable discussion of the Mechanical Equivalent of Heat.

Mr. J. Graham, after having retired from business, in somewhat delicate health, was induced, in 1861, to take charge of the issue of the new bronze coinage from the Mint. By this successful operation, the copper coinage of the United Kingdom has been improved in quality, doubled in quantity, and a balance of profit, amounting to £350,000, has at the same time been added to the Exchequer. On the demise of Professor Brande, three years ago, Mr. J. Graham was appointed his successor in the Coining Department of the Mint; and was engaged in devising new machinery for striking coins, when his useful career was brought to a termination. He died on the 22nd February, 1869.

Dr. William Bird Herapath was the eldest son of the late Mr. William Herapath, of Bristol, the well known toxicological chemist, whom he survived only eight months. For some years he assisted his father in the laboratory and medical school. Having studied at the Bristol Medical School and London Hospital, he took his M.B. degree in the University of London in 1844, with honours in six different branches; and seven years later he graduated M.D.; he was also a member of the Royal College of Surgeons. Dr. W. B. Herapath was a fellow of the Royal Societies of London and Edinburgh. His medical practice was extensive, but he nevertheless found leisure to contribute numerous papers to the medical journals, and to pursue his chemical investigations. In 1851 he discovered the peculiar optical properties of the crystals of iodo-quinine sulphate, which have received the name of

Herapathite, and which he proposed should be used as artificial tourmalines. In 1857 he published another result of these physico-chemical researches in a paper on the Cinchona Alkaloids. His last printed paper was on "The use of the Spectroscope and Micro-spectroscope in the discovery of Blood-stains and Dissolved Blood." During the summer of last year, when his health was fast failing, he devoted as much time as he could spare from his professional calls to the application of spectroscopic observation to the investigation of the chlorophyll of various plants, the unfinished results of this labour being yet unpublished. He died on the 12th of October, 1868, at the age of 48; although his death was unexpected, there was sufficient organic disease to render such an event imminent. In character Dr. Herapath was particularly generous and open-hearted.

Mr. Robert Porrett was born on the 22nd September, 1783; he died on the 25th November, 1868, at the age of 85. He was an original member of the Chemical Society, and was, to within a very short period previous to his decease, a constant attendant at its meetings, as well as at those of other societies to which he belonged. Mr. Porrett was for many years our Treasurer, and was, on more than one occasion, pressed to accept the Presidency, which he declined on the ground of his advanced age. He was elected a Fellow of the Royal Society in 1848; he was a Fellow of the Antiquarian and Astronomical Societies, and a member of the old Mathematical Society of Spitalfields, until its junction with the Astronomical Society. Few of our younger fellows recognized in the venerable visitor, a representative of their science at its very infancy, one who was a worker in chemistry before the birth of the atomic theory, and who was amongst the first to test the accuracy of the results of chemical analysis by comparing them with an atomic formula. In April, 1809, just sixty years ago, Mr. Robert Porrett, jun., received the medal of the Society of Arts for his discovery of *prussous acid*, which he had obtained by acting on compounds of prussic acid by "hydro-guretted sulphuret of potash." It must be recollected that the processes of analysis were not then in an advanced or trustworthy condition, and he was led to infer that, because he had employed a deoxidising reagent, he had obtained an acid containing less oxygen than prussic acid, which was then believed

to be an oxyacid. Subsequently, however, by persistent work, he arrived at the true composition of this acid, which he called "sulphuretted chyazic acid," and also of that of the so-called triple prussiates, which he proved to be compounds of an acid in which iron is intimately associated with the elements of prussic acid; this he called "ferruretted chyazic acid." In a paper in the Phil. Trans., 1814, entitled "On the nature of the Salts termed Triple Prussiates, and on Acids formed by the union of certain bodies with the elements of Prussic Acid," he says, "I propose, therefore, for the acid composed of the elements of the prussic acid, united with black oxide of iron, the name of *ferruretted chyazic acid*; for that composed of the same elements with sulphur the name of *sulphuretted chyazic acid*; for those consisting of the same elements with metallic oxides, analogous names, as argenuretted chyazic acid, &c., the word *chyazic* being composed of the first letters of the acidifiable elements of the acid, viz., carbon, hydrogen, and azote, to which is added the termination *ic*." The greater part of the period of Mr. Porrett's scientific activity was occupied in investigating and establishing the true composition of ferrocyanic and sulphocyanic acids. Between 1809 and 1819 he contributed several papers on this subject to the Philosophical Transactions and other scientific journals: in addition to that before cited, they are as follows:—"On Prussic and Prussous Acid," Trans. of the Soc. of Arts, vol. xxvii, 1809, p. 89; "Further Analytical Experiments relative to the Constitution of the Prussic, of the Ferruretted Chyazic, and of the Sulphuretted Chyazic Acids, and on that of their Salts; together with the application of the Atomic theory to the analysis of these Bodies," Phil. Trans., 1815, p. 220; "On the Anthrazothion of Von Grotthus, and on Sulphuretted Chyazic Acid," Thomson's Annals of Philosophy, vol. xiii., 1819, p. 356; "On the Triple Prussiate of Potash," Ann. Phil. vol. xii., p. 214, which contains a discussion of his own analyses of "ferruretted chyazic acid," and that of Dr. Thomson, published in a previous part of the same volume; "On Ferrocyanate of Potash, and on the Atomic Weight of Iron," Ann. Phil. vol. xiv., 1820, p. 205.

Besides the discovery of the hydro-ferrocyanic and hydro-sulphocyanic acids, which Mr. Porrett always looked back upon with a just feeling of pride, he was engaged in 1813 with Messrs. Wilson and Rupert Kirk, in a perilous investigation

of "the explosive compound of Chlorine and Azote" (*Nich. Journal*, vol. xxxiv., p. 180). This research was conducted with much acumen and boldness; it comprised the devising of several methods of preparing that compound, and a thorough examination of its physical properties, together with an attempt to analyse it by exploding it in a partial vacuum.

In 1816 he communicated to Thomson's *Annals of Philosophy*, vol. viii., p. 74, an account of "Two Curious Galvanic Experiments," in which he showed that a fluid is made to pass against gravity by the electric current through a membrane (bladder or paper saturated with albumin, which was subsequently coagulated) from the positive to the negative pole, when the conducting wires of eighty elements are connected with water placed at different levels on each side of the membrane. He also described the increase of action which is produced in an exhausted voltaic battery by removing a portion of the fluid, thus causing the still moist plates to be exposed to the action of the air.

In 1817 he made some "Observations on the Flame of a Candle," which were published in the *Annals of Philosophy*, vol. ix., p. 337. He investigated the phenomena of the combustion of a candle by inserting a piece of wire-gauze, cut nearly to the shape of the flame, and placed, so as to form a vertical section of it; also by inserting pieces of wire-gauze horizontally; and further by collecting and partially condensing the vapours by placing a small tube in various parts of the interior of the flame.

After a lapse of twenty-six years, he again, in 1846, at the age of sixty-three, took up chemical investigation, and contributed, in conjunction with the late E. F. Teschmacher, a paper "On the Chemical Composition of Gun Cotton," to the *Journal of our Society* (*Memoirs*, vol. iii., 1845—1848, p. 258). His last paper "On the existence of a new Vegeto-Alkali in Gun Cotton," for which he proposed the name of Lignia, was read before the Society on December 21st of the same year, and is printed in the *Memoirs*, vol. iii., p. 287.

Mr. Porrett was not a professional chemist; his scientific work was accomplished as an intellectual pastime, when, as he has expressed it in one of his papers, "leisure and inclination combined." Besides being a chemist, he was an antiquarian, and profiting by the facilities offered by his residence in the Tower,

he paid much attention to ancient arms and armour, with which he was intimately acquainted, and could at once detect an anachronism in their classification, or in the grouping of the components of a suit of armour made up for sale. Mr. Porrett's father held the office of Ordnance Storekeeper in the Tower, and occupied a house there. The subject of this memoir, when he was about eleven years old, used to amuse himself by drawing up and writing out official papers for his father; they were so well worded and written, that they attracted the attention of the officials at the War Office, and an offer was made to his father to keep him in his office as an assistant. With some hesitation this offer was accepted, and he remained in office for 55 years, having risen in course of time to be the chief of his department. On the occasion of his retirement, in 1850, he had the gratification of receiving a high testimonial from his superiors, and a complimentary address, together with a silver inkstand from his subordinate officers, by whom he was much beloved, as he was indeed by all who knew him intimately. Mr. Porrett lived and died a bachelor, but is represented by his nephews, Mr. J. F. Collier, of the Temple, and Sir Robert Porrett Collier, the present Attorney-General.

Christian Friedrich Schönbein was born October 18, 1799, at Metzingen, in Würtemberg. After receiving a good elementary education he was, when 14 years of age, apprenticed in a chemical manufactory at Böblingen, where he remained seven years, and during which period he, with great assiduity, devoted his leisure hours to the study of science. In 1820 he obtained a position in the chemical manufactory of Dr. Dingler, the editor of the well-known "Dingler's Journal," which afforded him an excellent opportunity for pursuing his scientific studies. It was during this time that he especially studied chemistry, mathematics, the Latin language, and philosophy, the latter being his favourite study. Shortly after this he went to Hemhofen, near Erlangen, where he directed the chemical factory of a Mr. Adam. The proximity of the university town of Erlangen caused him to pay frequent visits thereto, and he soon became an intimate friend of Pfaff, the professor of physics and mathematics, Schubert, the professor of zoology, and the well-known philosopher, Schelling. The acquaintance and intercourse with these men

had a marked influence upon his future career, and matured in him the resolution he had formed to give himself up entirely to the pursuit of scientific chemistry. He found the means to enable him to enter the university of Tübingen in 1821, where he studied under the Professors Gottlieb, Gmelin, and Bohnenberger. From Tübingen he went to Erlangen, where he completed his university education. After this he filled for a short time the post of teacher of chemistry and physics at the college of Keilhau, in Thuringia; and then he came to England, where he held a similar position for a year, in an educational establishment at Epsom; and a year he spent in London. In 1827 he went to Paris, in order to make himself acquainted with the scientific schools there, and attended during his sojourn principally the lectures of Gay-Lussac, Ampère, Despretz, and Thénard. In 1828 he received a call to the university of Basle, and in 1829 was made honorary doctor by the faculty of philosophy. In 1835 he became Professor *ordinarius* of physics and chemistry, a position he held until his death, the only change being that in 1852, when a special professorship for physics having been created, he retained the chair of chemistry.

In his capacity of professor, Schönbein exercised a marked influence upon his hearers by his clear and impressive style of delivery, and created thereby an active interest for science amongst his students. He was rather slow in shaping his views according to the prevailing theoretical notions of the day; being too much occupied with the pursuits in his own particular sphere, he could not find leisure to familiarize himself sufficiently with the speculations of others. Nevertheless, the want in this respect was amply compensated by the peculiar freshness with which he introduced the main results of his own researches in the generality of science, and by the light he threw upon other scientific subjects by considering their bearings from his own point of view.

His power to render the results of scientific discoveries in a popular comprehensive form gave him frequent occasions to deliver lectures before a larger public, and in this respect his activity at meetings of the Society of Naturalists of Basle, and those of the scientific associations of Switzerland and Germany must not be omitted.

Though essentially a man of science, Schönbein was of social habits, and fond of spending some of his leisure hours

in the society of his friends, where his geniality found a just appreciation. He likewise took part in the political affairs of the country, and was presented with the honorary citizenship of Basle. Subsequently he was made a member of the Council of the Canton in 1848, and became a member of the Great Council in 1851.

It is not possible to give here an account, or even a list, of the very numerous published memoirs of Schönbein.* The peculiar and individual mental development of Schönbein, which characterised him from his early youth, maintained throughout his life its influence upon his scientific pursuits. As early as 1836 we find his mind already occupied with the phenomenon at that time called isomerism, but which at a later period received the name of allotropy. The whole of his work is, so to speak, a continuous chain of observations, and it is very easy to trace how, step by step, each of his researches was suggested by those which had preceded it. His early labours were devoted principally to physico-chemical enquiries, such as chemical passivity, voltaism, and electrolysis. Although the publications of Schönbein during this period possessed a very considerable amount of scientific interest, yet it may be said fairly that it was by his discovery of Ozone, in 1839, that he attained his high position amongst the savants of the day. The peculiar odour perceptible during electric discharges had been already noticed under several circumstances, and Schönbein himself had paid some attention to it; but it was on the occasion of the meeting of the British Association at Birmingham, at which he was present, that the battery of Mr. Grove was first seen by him, and at once riveted his attention, as being likely by its powerful action to afford the means of furnishing this odorific principle in sufficient abundance for investigation. Having, with the aid of Messrs. Watkins, constructed such a battery of much larger dimensions than any made before, he very shortly succeeded so far with his experiments as to feel himself justified in announcing the discovery of Ozone. It would lead us too far to enter here more fully into the early history of this remarkable substance. The extraordinary difficulties which for a long time baffled the efforts of

* A valuable list of the papers contributed to science by Schönbein, will be found in a memoir communicated to the University of Basle, by Professor Edward Hagenbach.

many other chemists, besides Schönbein, to make out its true chemical nature are still fresh in our memory. The similarity of the chemical properties of Ozone with those of the peroxide of hydrogen led Schönbein to submit this substance, like many other peroxides, to his peculiar mode of examination, and the results which he derived from these researches developed his theory of the polarization of oxygen, according to which this element occurs in three different states, namely, as ordinary inactive oxygen, Ozone, and Antozone.

In intimate connection with the history of Ozone stands Schönbein's discovery of Gun-cotton, which in consequence of its application to photography, and by virtue of being a powerful explosive, has become one of the most important chemical substances.

Schönbein, though suffering occasionally from gout during the later years of his life, enjoyed otherwise very good health up to his decease. It was whilst on a visit to a friend at Sauersberg, near Baden-Baden, that he was suddenly taken ill, and died, after a few days' illness, on August 29, 1868.

During the past year, two resolutions have been passed by you, which cannot fail to promote the advancement of chemical science, and to increase the influence of our Society. The first is that sanctioning the application of part of our funds in aid of original investigation; the second the founding of the Faraday Lectureship and Medal, which will tend to make us personally acquainted with the most distinguished of our foreign brethren.

I beg to assure you that I shall always, on account of these events, and for many other reasons, look back with feelings of pride to the period of my Presidency. Before I quit this chair, which by your suffrages I have held for two years, permit me to offer you my heartfelt thanks for the kind support which I have at all times received from my colleagues on the Council, and from all the Fellows of our Society.

List of Papers read at the Meetings of the Chemical Society, between March 31st, 1868, and March 30th, 1869:—

1. "On the Constitution of Glyoxylic Acid:" by W. H. Perkin, F.R.S., and B. F. Duppa, F.R.S.
2. "On a Glyoxalic Amide:" by Dr. Odling, F.R.S.
3. "On the Occurrence of Organic Appearances in Colloïd Silica:" by Mr. W. Chandler Roberts.

4. "On the Solubility of Xanthine in Dilute Hydrochloric Acid:" by Dr. Bence Jones, F.R.S.
5. "Researches on New and Rare Cornish Minerals:" by Prof. A. H. Church.
6. "On an Improved Voltastat:" by Dr. Guthrie.
7. "On Graphic Formulæ:" by Dr. Guthrie.
8. "On the Tetraphosphoric Amides:" by Dr. J. H. Gladstone, F.R.S.
9. "On the Solubility of Plumbic Chloride in Water, and in Water containing Hydrochloric Acid:" by Mr. J. Carter Bell.
10. "Some Experiments on the Application of the Measurement of Gases to Quantitative Analyses:" by Dr. W. J. Russell.
11. "Observations on the Combining Powers of Carbon:" by Mr. W. H. Perkin, F.R.S.
12. "On the Reducing Action of Peroxide of Hydrogen and Carboic Acid:" by Mr. John Parnell.
13. Chemical Notices:—i. "On the Action of Chloride of Zinc in Oxalic Ether."—ii. "On the Artificial Production of Pyridine."—iii. "Isomerism in the Organic Cyanides:" by E. T. Chapman and Miles H. Smith.
14. "On the Modes of Testing Mineral Oils used in Lamps:" by Dr. B. H. Paul.
15. "Additional Note on Tetraphosphoric Amides:" by Dr. J. H. Gladstone, F.R.S.
16. "On High Chemical Formulæ—the ground on which they rest:" by Prof. Wanklyn.
17. "On the Production of Saltpetre in India:" by Dr. W. J. Palmer.
18. "On a New Instrument for Maintaining Constant Temperature:" by Dr. Guthrie.
19. "On Chalybite, Diallogite, and Woodwardite:" by Professor A. H. Church.
20. "On the Application of Chlorine Gas to the Toughening and Refining of Gold:" by Mr. Francis Bowyer Miller.
21. "Note on the Specific Gravity and Boiling Point of Chromyl Dichloride:" by Mr. T. E. Thorpe.
22. "Analysis of the Ashes of a diseased Orange Tree (*Citrus Aurantium*):" by Mr. T. E. Thorpe.
23. "On the Isolation of the Missing Sulphur Urea:" by Mr. J. Emerson Reynolds.
24. "On some Compounds of Phosphorus containing Nitrogen:" by Dr. J. H. Gladstone, Ph.D., F.R.S.
25. "Mineralogical Notices:" by Professor A. H. Church.
26. "Note on the Action of Chloride of Lime on Aniline:" by Mr. W. H. Perkin, F.R.S.
27. "On the connection between the Mechanical Qualities of

Malleable Iron and Steel, and the Amount of Phosphorus they contain:" by Dr. B. H. Paul, Ph.D.

28. "On the Chemical Composition of Canaüba Wax:" by Mr. Nevil Story-Maskelyne, M.A.
29. "On the Butyl Compounds derived from the Butylic Alcohol of Fermentation:" by Ernest T. Chapman and Miles H. Smith.
30. "On a certain Reaction of Quinine:" by Professor G. G. Stokes, F.R.S.
31. "On the Determination of the 'Total Carbon' in Cast-Iron:" by Mr. Arthur H. Elliott.

The following Lectures have also been delivered:—

1. "On the Regenerative Gas Furnace, as applied to the Production of Cast-Steel:" by Mr. C. W. Siemens, F.R.S.
2. "On the Chemistry of Sugar Refining:" by Dr. Wallace, F.R.S.E.
3. "On Catharism, or the Influence of Chemically Clean Surfaces:" by Mr. Charles Tomlinson, F.R.S.

The following Fellows were elected Officers and Council for the ensuing year:—

President.—A. W. W. Williamson, Ph.D., F.R.S.

Vice-Presidents who have filled the office of President.—Sir B. C. Brodie, F.R.S.; Warren de la Rue, Ph.D., F.R.S.; Thomas Graham, D.C.L., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; W. A. Miller, M.D., D.C.L., F.R.S.; Lyon Playfair, Ph.D., C.B., F.R.S.; Colonel P. Yorke, F.R.S.

Vice-Presidents.—J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; H. M. Noad, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; T. Redwood, Ph.D.; John Stenhouse, LL.D., F.R.S.

Secretaries.—A. Vernon Harcourt, M.A., F.R.S.; W. H. Perkin, F.R.S.

Foreign Secretary.—H. Müller, Ph.D., F.R.S.

Treasurer.—F. A. Abel, F.R.S.

Other Members of the Council.—E. Atkinson, Ph.D.; J. Lothian Bell; E. T. Chapman; W. Crookes, F.R.S.; David Forbes, F.R.S.; D. Hanbury, F.R.S.; A. Matthiessen, Ph.D., F.R.S.; E. J. Mills; J. Prestwich, F.R.S.; Maxwell Simpson, Ph.D., F.R.S.; A. Voeleker, Ph.D.; Greville Williams, F.R.S.

JOURNAL

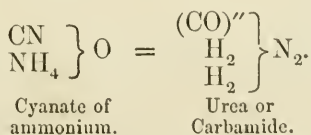
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THE CHEMICAL SOCIETY.

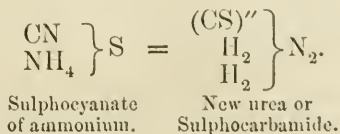
I.—On the Isolation of the Missing Sulphur Urea.

By J. EMERSON REYNOLDS, Member of the Royal College of Physicians, Edinburgh; Keeper of the Minerals and Analyst to the Royal Dublin Society, &c.

WHEN an aqueous solution of cyanate of ammonium is simply evaporated to dryness, the salt is well known to undergo isomeric change, thereby yielding a body which is identical in properties with ordinary urea. The alteration which takes place in this beautiful process of Wöhler's, is usually represented in the following way by those chemists who regard urea as carbamide, or diammonia in which two equivalents of hydrogen are replaced by the diatomic radicle CO" or carbonyl:—



Cyanate and sulphocyanate of ammonium (sulphocyanide of ammonium) are well known to be salts of very similar constitution: hence the sulphocyanate should yield, on heating, a corresponding urea containing sulphur, thus:—



In the latter case the radicle (CS)" takes the place of the carbonyl in ordinary urea.

Owing to the great probability of effecting this change, the action of heat on the sulphocyanate of ammonium has been made the subject of special study by Baron Liebig, Professor Völekel, and other chemists, but with negative results, so far as the discovery of the sulphur urea was concerned. Still more recently Dr. Hofmann, in pursuing his valuable researches on the compound ammonias, has prepared, indirectly, a number of substitution-products of the sulphur urea, though this distinguished chemist did not succeed in isolating the body itself, and hence appears to have adopted the hypothesis that sulphocyanate of ammonium is the sulphur urea, but possessing a peculiarly pronounced saline constitution.*

The object of the present communication is to show that the sulphur urea can not only be prepared directly from the sulphocyanate of ammonium, but that it can be obtained in considerable quantities by a process precisely similar to that discovered by Wöhler for the artificial preparation of the ordinary or oxygen urea.

An attentive consideration of the points of similarity and of difference between cyanate and sulphocyanate of ammonium was sufficient to convince me that the greater stability of the latter salt must be the chief obstacle to the molecular rearrangement of its constituents. We are familiar with the fact that it is only necessary to evaporate an aqueous solution of cyanate of ammonium to dryness at a boiling temperature, in order to convert it completely into ordinary urea. The temperature of boiling water is, therefore, sufficient to induce isomeric change in the case of the cyanate. But the sulphocyanate is unaffected by similar treatment, and though unaltered at 100° C., under ordinary circumstances, it decomposes easily when heated alone at temperatures beyond 180° C. I was led by these considerations to examine closely the action of heat upon the sulphocyanate between the above ranges of temperature, and have been amply rewarded by the isolation of the missing sulphur urea.

The following is the mode of operating which experience has shown me to give the best result.

About 500 grammes of *well dried* sulphocyanate of ammonium

* Proceedings of Royal Society, vol. ix, p. 274.

should be placed in a flask of suitable size, a thermometer then introduced, and the whole heated *gradually** by means of an oil-bath to a temperature of about 170°C. for two hours. I may here mention, incidentally, that the fusing point of the perfectly dry salt was found on repeated trials with large quantities of material, to be 159°C. , instead of 147°C. , as stated in the books, the error in the latter case probably arising from the presence of moisture in the sample examined. When the temperature of the fused mass is carefully adjusted to nearly 170°C. , but little ammonium sulphide is produced, and scarcely a trace of carbonic disulphide. When the mass has been kept in a state of fusion for a sufficient time, it is allowed to cool down, and when its temperature has reached 100°C. , it is treated with its own weight of warm water (80°C.); when the whole has dissolved the solution is filtered at once through a small plug of cotton, for the purpose of separating a black substance, always formed in small quantity, and then left to crystallise.

After some hours the liquid yields an abundant crop of fine, long, silky crystals, which sometimes cling together in a remarkable manner. The crystals are now to be drained off from the mother-liquor, and pressed between folds of bibulous paper, and again crystallised from as small a quantity of boiling water as possible. The urea now crystallises in fine prisms, but not thicker than an ordinary sewing-needle. Owing to the pertinacity with which the sulphocyanate adheres to the new substance, several crystallisations are needed before it is obtained in a state of purity.

When perfectly dried *in vacuo* over sulphuric acid, the crystals were found to contain carbon, hydrogen, nitrogen, and sulphur. Owing to the presence of a large proportion of nitrogen and of sulphur in the compound, considerable difficulty was encountered in the determination of the carbon; fortunately, this is of rather less importance than usual, since the remaining constituents admit of direct estimation. After many trials, the following modification of the ordinary process was found to be best suited to the particular case. A combustion tube was employed in each instance between 85 and 90 centimetres long. A few centimetres of pure dry chromate of lead having been

* When the perfectly dry sulphocyanate is very quickly heated to beyond the fusing point, a body analogous to Linneman's sulphocyanic anhydride appears to be produced, as I have pointed out in another place.

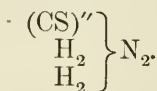
first introduced, an intimate mixture of the substance with warm chromate and then the rinsings of the mortar were added, so as to occupy about 30 centimetres; a layer of about 15 centimetres of plain chromate was now filled in, and a porous rod of copper occupied the anterior portion of the tube. The copper rod was obtained by rolling up *very closely*, fine copper gauze, so as to prepare a porous cylinder without any central tube. The rod so prepared was first heated in air, and then reduced in a current of hydrogen in the usual way, and when closely fitting to the combustion tube, was found to secure the complete reduction of the nitrogen oxides formed during the analysis. The combustion was conducted *very slowly*, and the temperature of the anterior layer of pure chromate of lead never allowed to get beyond a very low red heat.

The following are the results obtained:—

- I. .2774 grm. of the carefully dried and pure substance gave .13312 of water. Carbon determination a bad one.
- II. .3923 grm. gave .2295 of carbonic acid, and .18242 water.
- III. .259 grm. gave 1.524 grm. $(\text{NH}_4)_2\text{PtCl}_6$. And .5 grm. gave, on treatment by Carius' method, 1.531 grm. $\text{Ba}''\text{SO}_4$.
- IV. .5 grm. treated in the same way, gave 1.525 grm. $\text{Ba}''\text{SO}_4$.
The substance used in this estimation was crystallised from alcohol.

Calculated.			Found.			
			I.	II.	III.	IV.
Carbon. . . .	12	15.789	—	15.886	—	—
Hydrogen . .	4	5.263	5.330	5.166	—	—
Nitrogen. . .	28	36.843	—	—	36.891	—
Sulphur . . .	32	42.105	—	—	42.235	42.068
	<hr/>	<hr/>				
	76	100.000				

Analysis, then, leads well to the formula,—

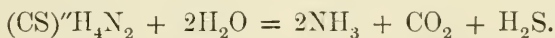


It will be presently seen that this formula is corroborated by the analyses of several well marked compounds of the new urea.

The new substance occurs either in long fine crystals, or in very short thick prisms belonging, in either case, to the rhombic system. The crystals are non-deliquescent in moderately dry air, easily soluble in water and alcohol, and but slightly soluble in ether. The particular form in which the urea is obtained from either alcoholic or aqueous solution, is dependent to a great extent on the presence or absence of impurities. The solution froths slightly on agitation, has a neutral reaction, and rather bitter taste.

When the urea is heated with water in a sealed tube for some hours to 140° C., it is reconverted into sulphocyanate of ammonium, as evidenced by the intense red colour struck by the liquid on testing with a ferric salt. The urea itself when quite pure does not give a colour reaction with this test.

When digested with hydrate of potassium in a sealed tube for some hours, at a temperature of 100° C., the substance afforded ammonia, sulphhydrate, carbonate, and a little sulphocyanate of potassium. The essential decomposition which takes place in the presence of an alkali may be represented thus—



The decomposition with sulphuric or hydrochloric acid is precisely similar to the foregoing.

When boiled with dilute nitric acid, the sulphur is easily oxidized to sulphuric acid. Nitrites and hypochlorites liberate nitrogen from the urea. When treated with a large excess of permanganate of potassium and alkali, by Wanklyn and Gangee's plan,* nitrogen is also set free, and the sulphur oxidized to sulphuric acid.

The fusing point of the new urea is 149° C. When gently heated upon platinum-foil, it fuses, and then volatilises without blackening or leaving a residue. When heated in a closed tube it fuses, then boils up, evolving sulphide of ammonium, carbonic disulphide, and ammonia (?); the mixture quickly blackens, but on continuing the heat, a yellow oil distils over, and a white mass is left in the tube. This residue strongly resembles Liebig's hydromellone.

When to a nearly saturated aqueous solution of the urea we add an excess of colourless nitric acid of specific gravity 1.25,

* Journ. Chem. Soc., vol. vi, p. 25.

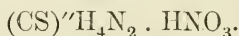
avoiding any rise in temperature, we obtain a beautiful crystalline nitrate, sparingly soluble in the presence of nitric acid. A quantity of the salt was prepared and freed from nitric acid by repeated pressure between folds of blotting paper, until the crystals were almost completely dried; the final desiccation was then rapidly effected in a current of dry air,* and the substance analysed immediately, since it rapidly decomposes.

Having satisfied myself of the persistence of the molecule of the sulphur urea, I found that the proportion of it existing in its compounds could be accurately determined by estimating the sulphur present and calculating this into urea. This is the plan pursued in most of the analyses which follow:—

- I. 1.0 grm. of the pure nitrate gave 1.6515 grm. $\text{Ba}''\text{SO}_4$, when treated by Carius' method. Very little heat is needed to effect the decomposition.
 II. 1.0 grm. gave 1.6603 $\text{Ba}''\text{SO}_4$.

	Calculated.		Found.	
			I.	II.
(CS)'H ₄ N ₂	76	54.67	54.22	54.39
HNO ₃	63	45.33	—	—
	<hr/>	<hr/>		
	139	100.00		

The results agree well with the formula.



I have not succeeded in obtaining a hydrochlorate of this urea.

1.0039 grms. of the dry substance, when subjected to a current of dry hydrochloric acid gas for two hours, at first without and afterwards with heat, did not undergo any apparent change, and increased in weight to the extent of .0103 grm.

I have not hitherto been able to prepare an oxalate.

Gold Compound.—If to a saturated aqueous solution of the pure sulphur urea, a nearly neutral solution of terchloride of gold be added very gradually, a yellow colour is soon developed

* I attempted to dry a quantity, of about 6 grammes, of the nitrate *in vacuo* over sulphuric acid, but after some hours drying, the whole suddenly decomposed with a slight explosion.

in the liquid. On the addition of each drop of the gold solution, a reddish precipitate appears, which quickly redissolves. The point to be reached is that at which fresh gold solution ceases to be decolorised *quickly*. The liquid, on slow evaporation, yields beautiful, pearly, monoclinic crystals, which, on recrystallisation, are obtained pure.

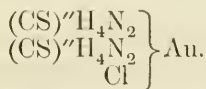
The crystals were found to contain the new urea, chlorine, and gold.

I. 2387 gave 12195 grm. of gold, on cautious ignition after previous treatment with nitric acid.

II. 6596 grm., treated with nitric acid, the liquid diluted, and precipitated by chloride of barium; 797 grm. Ba''SO_4 , obtained = 16.66 per cent. of sulphur. The filtrate was then evaporated nearly to dryness, with addition of sulphuric and hydrochloric acids; the solution, after sufficient dilution, was freed from the new precipitate of sulphate of barium, and the gold thrown down from the filtrate by ferrous sulphate. 33655 grm. was obtained.

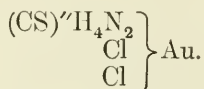
	Calculated.		Found.	
			I.	II.
Au.....	196.0	51.134	51.09	51.02
Cl	35.5	9.236	—	9.42 (by difference)
$2(\text{CS''H}_4\text{N}_2)$	152.0	39.630	—	39.56
	<hr/>	<hr/>		
	383.5	100.000		

I have therefore assigned to this salt the singular formula—



and we shall presently find that the composition of one of the platinum compounds proves the truth of the view which I now take of the constitution of this beautiful salt. All the ureas with which we are acquainted possess more or less decided basic characters, and, under certain conditions, very feeble acid functions also; but in the case of the new substance we have, I believe, the first instance of an urea which manifests very strongly marked acid functions, and correspondingly feeble basic characters.

In preparing the salt just described, it will be observed that the urea must be kept in excess, but when the gold solution preponderates, a reddish-yellow precipitate is produced, which decomposes so rapidly that it was found impossible to obtain it in a condition suitable for analysis; however, when we consider the constitution of the stable body already described, there appears to be some reason to believe that the red compound would turn out to be



if it could be separated in a state of sufficient purity for examination.

Platinum-compounds.—With platinum several compounds can be obtained. One of these bodies is highly characteristic of the new urea, and this I have studied with care.

When a solution of tetrachloride of platinum, containing as little free acid as possible is added to a slight excess of the aqueous solution of the sulphur urea, a bulky, highly crystalline, red precipitate is produced. The appearance of the precipitate is remarkable, and under the microscope the compound is well characterised by the peculiar plumose appearance of the long prismatic crystals. The precipitate when produced as described, must be quickly washed, first with water and then with alcohol. After pressing between folds of bibulous paper it must be rapidly dried at a temperature not exceeding 80° C. This platinum compound decomposes easily if left moist for some time, but keeps very well when thoroughly dry and free from tetrachloride of platinum.

In the present instance I did not consider it safe to determine the sulphur and platinum only, but sought for direct evidence of the permanence of the molecule of the sulphur urea by the estimation of the nitrogen and chlorine in addition.

Different preparations of the same salt were used in the following analyses:

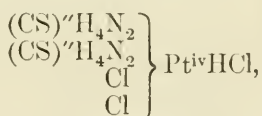
- I. .5265 grm. of a very carefully prepared and quickly dried sample gave .2268 grm. Pt.
 .4035 grm. gave when oxidized with nitric acid .4 grm. Ba"SO₄.
- II. .2729 grm. of another specimen gave, on ignition, .1172 grm. Pt.

III. .5374 grm. was cautiously fused with crystallised hydrate of barium, and small fragments of nitrate of ammonium added until no further action was produced; the mass was then digested with water, an excess of dilute nitric acid added, the solution filtered, and the chlorine determined in the filtrate; .4909 grm. of AgCl was obtained. A slight loss was unavoidable.

.5045 grm. after ignition with soda-lime gave .9872 $(\text{NH}_4)_2\text{PtCl}_6$.

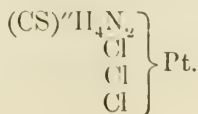
Calculated.			Found.		
			I.	II.	III.
Pt.	197.0	43.15	43.18	42.94	—
Cl ₃	106.5	23.33	—	—	22.62
S ₂	64.0	14.03	13.95	—	—
N ₄	56.0	12.26	—	—	12.22
C ₂	24.0	5.26	—	—	—
H ₉	9.0	1.97	—	—	—
	<hr/> 456.5	<hr/> 100.00			

The analysis leads well to the formula



thus according in constitution with the equally well defined gold salt.

If instead of adding a nearly neutral solution of tetrachloride of platinum to an excess of the sulphur urea in aqueous solution, we add the latter to an excess of platinic chloride containing free hydrochloric acid, we get but little if any precipitate till after the lapse of some time; then a dirty brown precipitate gradually deposits, which is freed from excess of platinic chloride with difficulty. A specimen so prepared, washed until incipient decomposition was observed, and then dried, gave 52.38 per cent. of metallic platinum. The formula



requires 51.97 per cent. of platinum. However, though there is considerable probability of the truth of the above formula for the dirty brown platinum salt, I only wish to be understood as suggesting it here, since this substance and two other platinum salts which the urea is capable of affording, require further investigation. I can only add that I have not succeeded in obtaining any platinum compound corresponding to the ordinary double salt of the metal.

Silver Compound.—When a solution of nitrate of silver is added to one of the urea, and the mixture heated, the precipitate first formed dissolves, but sulphide of silver quickly separates in flakes unless some free nitric acid be present. When the clear hot solution containing free acid is allowed to cool, a mass of coherent silky needles makes its appearance and must be collected, drained well, and recrystallised from water containing free nitric acid. When well dried by pressure, the desiccation must be rapidly completed in a current of dry air at ordinary temperatures. Even when adopting these precautions, it is impossible to prevent slight decomposition, since the presence of a small quantity of nitric acid appears to be essential to the stability of the compound.

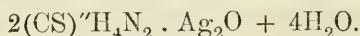
The following are the analytical results :—

I. .572 grm. of the salt gave .5701 grm. $\text{Ba}''\text{SO}_4$. And .867 grm. gave .5391 grm. AgCl .

II. .4879 grm. gave .3003 grm. AgCl .

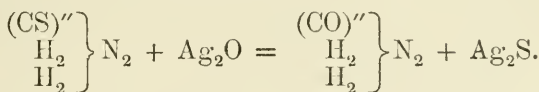
	Calculated.		Found.	
			I.	II.
$2(\text{CS})''\text{H}_4\text{N}_2$	152	33.33	32.63	—
2Ag	216	47.36	46.80	46.33
O	16	19.31	—	—
$4\text{H}_2\text{O}$	72			
	<hr/> 456	<hr/> 100.00		

These figures agree tolerably well with the formula.



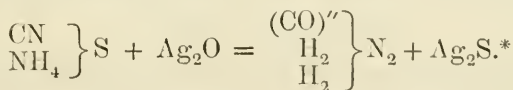
When the compound is gently heated in a tube, water is evolved, and, on increasing the heat, a slight explosion occurs with formation of sulphide of silver and the production of a crystalline sublimate.

Owing to the facility with which this urea yields up its sulphur to silver or other metal when the liquid is neutral or alkaline, I attempted the conversion of the new substance into the ordinary or oxygen urea in accordance with the following equation :



For this purpose quantities of the sulphur urea and of hydrate of silver, in accordance with the foregoing equation, were gently heated together with a little water for half an hour. The solution was then filtered from the sulphide of silver which had formed. The liquid left on evaporation a rather deliquescent crystalline residue, which was dissolved in alcohol; on evaporation of the alcoholic solution, fine prismatic needles were obtained. When the crystals were dissolved in water, and Liebig's test solution of mercuric nitrate added, a white precipitate was immediately obtained, which disappeared on running in solution of chloride of sodium. A sparingly soluble oxalate was also prepared and a nitrate. From the foregoing observations I conclude that the sulphur urea described in this paper, when treated with silver oxide, yields ordinary urea and sulphide of silver.

There is a process for preparing carbamide, which is but little known, and consists in heating a solution of sulphocyanate of ammonium with oxide of silver, the equation generally supposed to express the change which ensues being as follows :



We have now good reason to believe that this is but an incomplete expression of the change, since there can be little doubt that, in the first stage of the reaction, sulphur urea is produced, and this is subsequently attacked by the silver oxide as already pointed out.

The physiological interest attached to the question of the conversion of the new urea into the well known oxygen compound, is so considerable that I intend making it the subject of special enquiry.

* Naquet's Chemistry, translated by Curtis, p. 708.

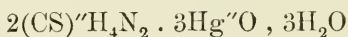
Mercurial Salts.—Several compounds of the sulphur urea with mercuric oxide and its salts appear to exist; of these, however, I will at present notice but one.

When nearly neutral solution of mercuric nitrate (Liebig's test) was added to a somewhat dilute solution of the sulphur urea, a precipitate was not immediately formed, but a crystalline body was ultimately thrown down, which, when washed and dried, gave the following results:

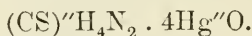
- I. 1.1894 grm. of the compound when treated with chlorate of potassium and hydrochloric acid, gave .5282 grm. of $\text{Ba}''\text{SO}_4$; and .9376 grm. gave on ignition in a tube in the usual way, with pure lime, .6627 grm. Hg.
- II. .718 grm. gave .50425 grm. Hg.

	Calculated.		Found.	
			I.	II.
$2((\text{CS})''\text{H}_4\text{N}_2)$	152	17.79	15.46	—
$3\text{Hg}''\text{O}$	648	75.88	76.35	76.2
$3\text{H}_2\text{O}$	54	6.33	—	—
	<hr/> 854	<hr/> 100.00		

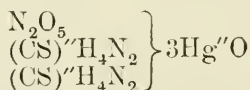
It would thus appear that the formula



is the correct one for this body, as I have reason to believe that this substance loses urea and water on prolonged washing, and becomes



When the mercuric nitrate is largely in excess the compound



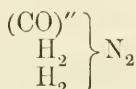
appears to be formed.* But I do not pursue the subject further here, since the composition of some of these metallic salts requires special investigation, and sufficient proof has now been given of the accuracy of the formula which I have obtained for the sulphur urea itself.

* The construction adopted in the text is employed for the purpose of exhibiting the relation of the compound to one of the basic mercuric nitrates which the well-known researches of Sir Robert Kane have made us acquainted with.

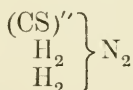
General Observations.—It will be easily perceived from the foregoing statements that the new urea described in this memoir must now take the place hitherto assigned to the sulphocyanate of ammonium, the latter salt falling back into its true position as the strict chemical analogue of cyanate of ammonium.

This change of idea is rendered necessary since some chemists—finding that Liebig and Völekel failed in converting the sulphocyanate of ammonium into the sulphur urea—have regarded the latter body and the sulphocyanate as identical, not only in centesimal composition, but in constitution likewise.

If we regard the oxygen urea as carbamide



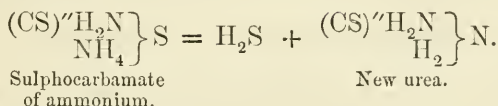
we must consider the sulphur urea as sulphocarbamide—



and we then have the new body as the primary of the following compound ureas, which have been discovered from time to time by Dr. Hofmann in his fine researches on the polyammonias.

Sulphocarbamide	$\left. \begin{array}{c} (\text{CS})'' \\ \text{H}_2 \\ \text{H}_2 \end{array} \right\} \text{N}_2.$
Allyl-sulphocarbamide..... ..	$\left. \begin{array}{c} (\text{CS})'' \\ \text{C}_3\text{H}_5 \\ \text{H}_3 \end{array} \right\} \text{N}_2.$
Allyl-naphtyl-sulphocarbamide	$\left. \begin{array}{c} (\text{CS})'' \\ \text{C}_3\text{H}_5 \\ \text{C}_{10}\text{H}_7 \\ \text{H}_2 \end{array} \right\} \text{N}_2.$
Ethyl-allyl-sulphocarbamide	$\left. \begin{array}{c} (\text{CS})'' \\ \text{C}_2\text{H}_5 \\ \text{C}_3\text{H}_5 \\ \text{H}_2 \end{array} \right\} \text{N}_2.$
Phenyl-sulphocarbamide	$\left. \begin{array}{c} (\text{CS})'' \\ \text{C}_6\text{H}_5 \\ \text{H}_3 \end{array} \right\} \text{N}_2.$

then sulphocarbamate of ammonium should yield the sulphur urea in a similar way.



I have little doubt that this idea will be realized if sufficient care be taken in conducting the experiment.

Laboratory, Royal Dublin Society,
December 3rd, 1868.

II.—On some Compounds of Phosphorus containing Nitrogen.

By J. H. GLADSTONE, Ph.D., F.R.S.

THREE series of acid bodies, all phosphoric amides, have been described in previous papers. They are respectively,

The Pyrophosphoric Amides.*

Pyrophosphamic acid	$\text{P}_2(\text{NH}_2)\text{H}_3\text{O}_6$.
Pyrophosphodiamic acid	$\text{P}_2(\text{NH}_2)_2\text{H}_2\text{O}_5$.
Pyrophosphotriamic acid.	$\text{P}_2(\text{NH}_2)_3\text{HO}_4$.

The Tetraphosphoric Amides.†

Tetraphospho-tetramic acid	$\text{P}_4(\text{NH}_2)_4\text{H}_2\text{O}_9$.
Terammoniated tetraphosphodiamic acid. .	$\text{P}_4(\text{NH}_2)_2\text{N}_3\text{H}_{13}\text{O}_{11}$
Tetraphospho-pentazotic acid	$\text{P}_4\text{N}_5\text{H}_9\text{O}_7$.

The Thio-phosphoric Amides.‡

Thio-phosphamic acid	$\text{P}(\text{NH}_2)\text{H}_2\text{SO}_2$.
Thio-phosphodiamic acid	$\text{P}(\text{NH}_2)_2\text{HSO}$.

During the investigation a number of other compounds have

* Quart. Journ. Chem. Soc., February, 1868, et. al.

† Ibid., July, 1868, et. al.

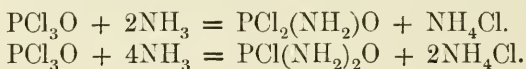
‡ Ibid., January, 1865.

been noticed, and more or less fully examined,—and I now propose to group together these miscellaneous observations.

Amidated Oxychlorides of Phosphorus.

When oxychloride of phosphorus is exposed to a slow current of ammonia gas, at a temperature of 0° centigrade, it combines to form a solid white body, and in so doing increases in weight about 22 per cent. This indicates the absorption of two molecules of ammonia; but on standing at the ordinary temperature the smell of the oxychloride always reappears, and the continuous passage of ammonia even at zero will cause a further increase of weight. At a higher temperature the combination proceeds much more rapidly, and the increase through absorption amounts to about 44 per cent. In either case the solid mass cakes together, and it is necessary to break it up frequently in order to insure the saturation of the oxychloride.

The most natural supposition is, that the ammonia removes one or two equivalents of the chlorine, their place being filled by amidogen, thus :



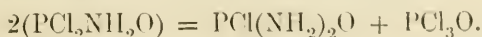
The increase in weight in the first case should be 22·15 per cent., in the second 44·3 per cent.

That this is really the case is a matter of which there can be little doubt, though all my efforts to separate either amidated compound from the chloride of ammonium have been fruitless. Water decomposes them at once, giving rise to pyro- or tetraphosphoric amides, and absolute alcohol decomposes them in some other manner, while no other solvent presented itself which was capable of dissolving the one and not the other substance. Still a mixture of alcohol and water was found to effect a partial separation. Thus when a portion of PCl_3O combined with 4NH_3 was washed with small quantities of ordinary methylated spirit, a great deal of chloride of ammonium was dissolved at once, but for a long time the insoluble portion continued to yield some chloride of ammonium, leading to the conviction that it was slowly formed; the long washed substance was divided into two portions; one was heated *per se*, and gave off ammonia and chloride of ammonium, while the

other was treated with water, which decomposed it at once, with the evolution of heat, and the production of the usual amidated acids, together with chloride of ammonium. Some of the substance resulting from the action of ammonia and oxychloride of phosphorus was washed with absolute alcohol; a portion dissolved with evolution of heat, while there remained what proved to be almost pure chloride of ammonium. The alcoholic solution evaporated to dryness in vacuo, and re-dissolved in water, showed that some compound ether of an aromatic odour had been formed, and it gave no indications of either ortho- or pyrophosphoric acid, or the amides of the latter, but rather of metaphosphoric acid; chlorine was also present. It has already been stated that when the compound of oxychloride of phosphorus and four equivalents of ammonia is heated at or above 200° centigrade, its constitution is so altered, that it gives a different acid amide on the addition of water. Some of this was washed with absolute alcohol till the chloride of ammonium was gradually but completely removed; there remained a white powder, which, when treated with water, gave the tetraphosphopentazotic acid, while the solution gave some indication of pyro-diamic and hydrochloric acids. These three experiments all show a separation of the white powder into chloride of ammonium, and some other chlorinated body, but in no case was the amide obtained in a state fit for analysis; in the last instance the small amount of chlorine (6.67 per cent.) showed that the transformation into an acid amide had been partially effected during the washing with alcohol.

The transformations of these amidated oxychlorides under the influence of water have been described in previous papers.

If the white powder produced by the treatment of oxychloride of phosphorus with more than two, and less than four, equivalents of ammonia, be allowed to stand for some time, the smell of the oxychloride develops itself, and if it be heated, the reproduction of this substance is still more evident. It would seem probable, therefore, that the lower compound is capable of transforming itself slowly into the higher compound and the original oxychloride:



The last atom of chlorine cannot be replaced by treating the

powder with gaseous ammonia at any temperature short of that at which the substance itself is decomposed,—above 300° centigrade. Indeed I have never succeeded in preparing such a substance as Schiff's phospho-triamide.

Phosphonitryle.

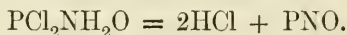
If the mixtures of amidated oxychloride of phosphorus and chloride of ammonium above described, be strongly heated, they give up all their chlorine and hydrogen, and part of their nitrogen, leaving behind a white amorphous substance, fusing at a bright red heat, incapable of combining with either acids or bases, and difficult of decomposition. This is the substance which has been described by various names, and has the composition PNO. That it was really this substance has been proved both directly and indirectly.

A portion of the mixture $\text{PCl}_2(\text{NH}_2)\text{O} + \text{NH}_4\text{Cl}$, when heated, gave off chloride of ammonium and hydrochloric acid, and lost 32·45 per cent.; the theoretical loss should have been 32·36 per cent.

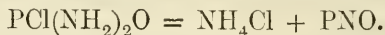
0·289 gramme of the residue fused with nitre and carbonate of sodium gave 0·525 gm. of pyrophosphate of magnesium. This agrees with the calculated amount.

	Calculated.	Found.
Phosphorus	50·82	50·73
Nitrogen	22·95	—
Oxygen	26·23	—
	100·00	

The decomposition will be as follows:—

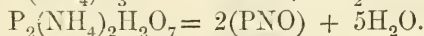
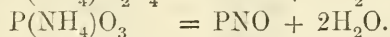
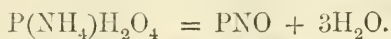


The same substance is produced when the higher amide is decomposed by heat, in which case the decomposition will be—



As Gerhardt's original name, bi-phosphamide, will be generally considered inapplicable to a substance of such a composition, I suggest the name phosphonitryle. PNO may be

theoretically derived from the ammonium salt of any variety of phosphoric acid by the subtraction of all the hydrogen in the form of water:



An attempt to prepare it by heating the pyrophosphate of ammonium gave a negative result.

Pyrophosphonitrylic Acid.

According to the notes of my assistant, the late J. D. Holmes, a series of bodies having the composition of pyrophosphonitrylates may be prepared by heating pyro-triamates. His analyses were very satisfactory, but in repeating the experiments I have never succeeded in obtaining the same results; at any rate the substances prepared by me have never been pure. The following account therefore must be understood as resting on the authority of his notes.

“Pyrophosphotriamate of potassium when ignited evolves two equivalents of ammonia, $\text{P}_2\text{N}_3\text{H}_6\text{KO}_4 = \text{P}_2\text{NKO}_4 + 2\text{NH}_3$, leaving a residue which may be considered as the potassium salt of a new acid, pyrophosphonitrylic (P_2NHO_4). This salt is a fused transparent glass, quite insoluble in water; when ground to a very fine powder in an agate mortar, and diffused through water, it is decomposed by a solution of AgNO_3 being deposited as a white heavy precipitate, which becomes converted on standing into microscopic crystals.”

In his experiment, 0.684 grm. lost 0.073, that is 10.6 per cent. In my experiment 0.892 grm. lost 0.097, that is 10.8 per cent. This is not in accordance with the formula given above, which will require a loss of 15.9 per cent.

Mr. Holmes gives the analysis of the silver salt and an analogous copper salt.

- I. 0.4325 of the silver salt gave 0.2445 of chloride of silver, and 0.4295 of the ammoniochloride of platinum.
- II. 0.4055 gave 0.2305 of chloride of silver.

These results give numbers not very different from those of the formula P_2NAgO_4 —

	Calculated.	Found.	
		I.	II.
Phosphorus..	25.00	—	—
Nitrogen....	5.65	6.22	—
Silver	43.55	42.54	42.78
Oxygen	25.80	—	—
	<hr/>		
	100.00		

0.345 grm. of the copper salt gave 0.0785 of oxide of copper, and 0.4405 of ammoniochloride of platinum, which agrees well with the formula P_2NCuO_4 —

	Calculated.	Found.
Phosphorus....	36.13	—
Nitrogen	8.16	8.00
Copper	18.41	18.15
Oxygen	37.30	—
	<hr/>	
	100.00	

If pyrophospho-triamic acid itself be heated at a low redness, it gives off ammonia without any water. Mr. Holmes found that 0.6585 grm. lost 0.065, that is 9.87 per cent. In my experiment 1.555 grm. lost 0.145, that is 9.3 per cent.

$P_2N_3H_7O_4 - NH_3$ requires 9.71 per cent. loss.

The residue was a semi-fused grey mass, insoluble in water, but gradually decomposed by that substance, even by the moisture of the air, which resolves it into a mixture of acid amides and ammonium salts, in which pyrophosphamic acid is most prominent, but in which may also be detected the tetraphosphoric compounds precipitable by alcohol. Mr. Holmes gives the following analysis of the residue :

I. 0.275 grm. gave 0.7715 of ammoniochloride of platinum.

II. 0.312 grm. gave 0.4375 of pyrophosphate of magnesium.

Which agree with the formula $P_2N_2H_4O_4$.

	Calculated.	Found.	
		I.	II.
Phosphorus..	39.24	—	39.15
Nitrogen....	17.72	17.55	—
Hydrogen ..	2.53	—	—
Oxygen	40.51	—	—
	<hr/>		
	100.00		

This may be considered as the pyrophospho-nitrylate of ammonium $P_2N(NH_4)O_4$, but I did not succeed in decomposing it by hydrochloric acid into NH_4Cl and P_2NHO_4 as I hoped.

Its resolution into pyrophosphamic acid is what might be anticipated of a nitrylate: $P_2N(NH_4)O_4 + 2H_2O = P_2NH_5O_6 + NH_3$.

Action of heat on Terammoniated Tetraphospho-pentamic Acid.

If this semi-fluid acid be heated *per se* at $100^\circ C$., it gradually gives off ammonia and something which has a smell resembling nicotine, and becomes a white brittle solid, dissolving in water from which alcohol throws down no precipitate. The result seems to be principally pyrophosphamate of ammonium. If it be heated at a higher temperature, some pyrophospho-triamic acid is also produced. If, however, the experiment be conducted at a temperature of about $220^\circ C$., ammonia is given off as before, and the resulting solid white mass is resolvable by cold water into two portions; in the solution are found pyrophospho-diamic and perhaps tetraphospho-tetramic acids; undissolved is an amorphous solid which is very sparingly soluble in cold water, but is instantly dissolved by warm water, or by cold dilute solutions of mineral acids, giving rise to pyrophospho-diamic acid.

0.252 grm. of the substance not dissolved by cold water gave 0.57 of ammoniochloride of platinum, and 0.292 of pyrophosphate of magnesium.

This agrees best with the simple formula PNH_4O_3 :

	Calculated.	Found.
Phosphorus	31.96	32.36
Nitrogen	14.43	14.18
Hydrogen	4.12	—
Oxygen	49.49	—
	<hr/> 100.00	

but as this substance is most easily resolvable into $P_2N_2H_6O_5$ and H_2O , it seems necessary to double, if not quadruple, the above formula. If we allow ourselves to speculate, we may imagine it $P_4N_4H_{14}O_{11}$, that is the semi-fluid acid $P_4N_5H_{17}O_{11}$, from which NH_3 has been driven by heat.

Tetraphospho-tetrimic Acid.

It has been previously shown, in describing the reactions of tetraphospho-pentazotic acid, that under the influence of nitrate of silver, it is broken up, with formation of tetraphosphotetrimate of silver. It has since occurred to me that this reaction might have a further bearing on the rational constitution of this body than was seen at first. If the silver salt merely transforms it from $P_4N_5H_9O_7$ to $P_4N_4H_4Ag_2O_7$ by the elimination of NH_3 as well as the basic hydrogen, the pale yellow salt should be to the original compound in the ratio of 315 to 512, or as 100 to 162.5. But if the tetrimic acid $P_4(NH)_4H_2O_7$ pre-exists in the compound in combination with $P_4N_6H_{12}O_7$, only about half that amount of silver salt will be produced, and the solution will contain the soluble products of decomposition of the hexamide. On performing the experiment, the silver salt actually obtained showed an increase of 50.1 per cent. on the original compound. This falls little short of the theoretical 62.5, and indicates that the reaction must have been of the character described in the first instance. On removing the excess of silver from the solution, it did give the usual reactions of tetraphospho-tetramic and pyrophospho-diamic acids, as well as ammonia, but these were probably secondary products of decomposition due to the slight excess of nitric acid.

If the views already given of the tetraphosphoric amides be correct, other bodies of a similar character might doubtless be prepared; indeed during the progress of the research, indications of such have been met with, but their reproduction and separation from one another are attended with extreme difficulty.

III.—*Mineralogical Notices.*

By A. H. CHURCH.

1. *Analysis of a Meteorite from South Africa.*

THE meteorite, or rather aerósiderite, which forms the subject of the present note, is reported as having been seen to fall on

the 20th of March in the present year. The locality of the fall is given as about two days' journey N.N.E. of Griqua Town, at a place known as Daniel's Knil. The native, a Griqua, who saw it fall near his hut, said it smelt strongly of sulphur, and was warm when he picked it up. It was offered by this man to the Rev. James Good, a missionary in Griqua Town, and finally given to a Griqua chief—Captain Nicolas Waterboer; from Captain Waterboer, Mr. J. R. Gregory obtained it.

This meteorite was of small size, weighing about 2 lbs. 5 oz. There is a crust upon it, having a dark grey colour, here and there speckled with reddish brown spots: these spots, resulting from the partial oxidation of the ferruginous materials of the stone, are more conspicuous a little way beneath the crust.

The ground-mass of this meteorite appears under the microscope to be greyish and yellowish white. Pretty uniformly distributed throughout its substance are numerous small particles, grains, and bunches of nickel-iron, presenting its usual metallic appearance. Two other minerals may also be detected in this meteorite, namely the ferrous sulphide known as troilite, and the somewhat undetermined species called schreibersite.

The density of this meteorite is rather low, considering the large quantity of metallic iron which it contains. Two determinations of the specific gravity gave the following numbers:—

$$1. D = 3.657.$$

$$2. D = 3.678.$$

I think it likely that the pieces with which I experimented contained minute air-cavities; they were also not free from ferric oxide arising from partial alteration.

In order to analyse the meteorite, it was finely powdered and digested in the cold with dilute hydrochloric acid; by this treatment the nickel-iron and troilite were dissolved; the quantity of the latter sulphide present was very evident, the first portion of the hydrogen evolved by the acid being much mixed with sulphuretted hydrogen. It was found that acetic acid also was capable of decomposing the troilite. The iron and nickel present in the acid solution were separately determined, while the sulphur was estimated by a separate experiment, the mineral being oxidized by nitric acid and potassium chlorate, and then the sulphuric acid formed, weighed as barium sulphate.

Several attempts were made to determine the schreibersite in the meteorite. It was approximately estimated by calculating its amount as being ten times that of the unoxidized phosphorus in the stone; this method gave uniform results.

The final results of the analysis of several small fragments of the meteorite were as follows:—

Nickel-iron	29.72
Troilite, calculated as FeS.	6.02
Schreibersite	1.59
Silica and Silicates	61.53
Carbon, Oxygen, other constituents, and loss.						1.14
						<hr/> 100.00

The nickel-iron alluded to above contained the following proportions of nickel and iron:—

Iron	94.72
Nickel	5.18

It appears from other analyses which I have made, that the nickel-iron in this stone is not distributed with perfect uniformity throughout its mass. One fragment gave me 2.03 per cent. of metallic nickel as existing in 100 parts of the meteorite; a proportion which would correspond to 37.17 per cent. of metallic iron, or 39.20 of nickel-iron.

The silicates of this meteorite are chiefly olivine and labradorite, the former species constituting by far the larger proportion of the powder unaffected by dilute acids. In two portions of the same sample, the silicates, after deducting the schreibersite, &c., amounted to

61.53 per cent.
61.10 „

In the analysis of another fragment, the silicates were found not to exceed 48.99 per cent.

2. *Action of Salt on Chessylite.*

In 1864 I commenced a series of experiments on this subject. I hoped to elucidate the formation of atacamite when sea-

water acts on copper ores. The only really successful experiment, was one in which the following substances had been placed together:—

200 cub. cent. of a 10 per cent. solution of pure salt, gave 2 grms. of chessylite.

The blue colour of the finely powdered chessylite slowly disappeared, a pale green tint taking its place, while at the same time the saline solution became notably alkaline from the conversion of the sodium chloride into carbonate. In the following table, the composition of chessylite, of its chlorinated product, and of atacamite are compared together:—

	$2\text{CuCO}_3, \text{CuH}_2\text{O}_2$ Chessylite.	$2\text{CuCl}_2, 9\text{CuH}_2\text{O}_2, 3\text{Aq. (?)}$ Chlorinated product.	Atacamite.
CuO	69·2	59·55	53·6
CO ₂	25·6	—	—
H ₂ O	5·2	18·14	16·2
Cu	—	10·47	14·3
Cl	—	11·70	16·0

IV.—*Note on the Action of Chloride of Lime on Aniline.*

By W. H. PERKIN, F.R.S.

ABOUT twelve years ago, when studying the process of converting aniline into aniline purple by means of bichromate of potassium, I very naturally made experiments also upon the oxidation of aniline by means of chloride of lime, to see if the colour of the reaction pointed out by Rungè was really due to aniline purple or not; but the results I obtained were of so decidedly negative a character that I did not pursue the inquiry very far, especially as my time was then much occupied.

Two or three years after the aniline purple had been introduced commercially, French manufacturers began to experiment upon this colouring matter, and succeeded in preparing it by oxidizing aniline with chloride of lime.

This fact puzzled me very considerably, but by following their process, I found that they were correct, and that aniline purple could be produced by means of a salt of aniline and chloride of lime; but I was at that time unable to look more fully into the matter, though I could not believe that my previous conclusions were erroneous. Lately I had the curiosity to repeat my original experiments, and was pleased to find they gave confirmatory results.

Runge, it will be remembered, designated aniline kyanol, or blue oil, on account of the blue reaction it gave with chloride of lime. If this reaction be performed properly, Runge's statement is found to be perfectly correct; but if too much chloride of lime be employed, brown products are likewise produced and these, when mixed with the blue, give an impure purple colour.

In making this experiment it is best to use a solution of hydrochlorate of aniline and a very dilute solution of chloride of lime, adding the latter reagent in small quantities at a time; by this means a dark slightly opaque indigo coloured solution is obtained. The dull appearance of this solution is due to the presence of suspended colouring matter, and if it be mixed with about its own bulk of alcohol it becomes perfectly clear and of a bright blue colour, like that of ammoniacal sulphate of copper, but in no way similar to that of aniline purple.

I have made a few experiments for the purpose of isolating this blue colouring matter, and have succeeded tolerably well.

If a large quantity of a cold dilute solution of hydrochlorate of aniline be treated with a very dilute solution of chloride of lime, so as to produce as much of the blue product as possible, and then saturated with chloride of sodium, the colouring matter is precipitated and may be collected upon a filter. This product is of a black colour, and very impure; when pressed it forms a soft, pitchy mass. It may be purified, however, by treatment with *cold* ether or benzol, which removes brown resinous bodies.

The product thus obtained dissolves in alcohol, producing a very fine blue solution. I therefore propose to call it *Runge's blue*. Its solution when evaporated on a glass plate, leaves the colouring matter with a coppery coloured surface.

Runge's blue is the salt of an organic base, possessing properties quite different from those of mauveine. The blue

alcoholic solution when mixed with hydrate of potassium changes to a reddish brown colour, but is reconverted into blue by the addition of an acid. An alcoholic solution of a salt of mauveine, when treated with caustic alkali, gives a violet reaction.

The sulphate of this blue colouring matter appears to be difficultly soluble in water.

The instability of this product has prevented me from getting it into a sufficiently pure state for analysis.

Runge's blue dyes silk of a blue or blue violet shade, but does not possess such an affinity for this material as a salt of mauveine.

It will be asked—if a solution of hydrochlorate of aniline produce Runge's blue with chloride of lime, how is it that manufacturers produce aniline purple with the same reagent?

The answer to this is, that the manufacturer goes a step further, and boils his product.

I find that an alcoholic solution of Runge's blue, when heated, rapidly decomposes, with formation of aniline purple, which may be obtained in crystals upon the addition of a little sulphuric acid. This change likewise takes place in the cold, after the lapse of twenty-four hours.

This decomposition can very well be shown by dyeing a piece of woven silk with Runge's blue, and then exposing it in parts to the action of steam, when the parts so treated will change in colour from blue to that of aniline purple. Exposure to heat will also produce the same result.

Therefore Runge's reaction does not produce aniline purple, but a blue colouring matter, which decomposes when heated, yielding a salt of mauveine.

V.—*Researches on Acids of the Lactic Series.*—No. I. *Synthesis of Acids of the Lactic Series.*

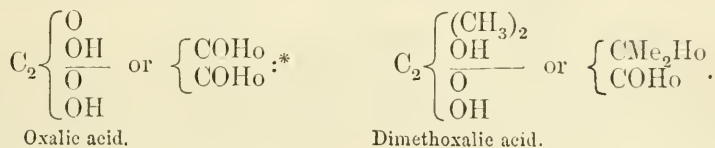
By E. FRANKLAND, F.R.S., Professor of Chemistry in the Government School of Mines; and B. F. DUPPA, Esq., F.R.S.

(From the Philosophical Transactions for 1866.)

WITH the exception of the acetic series, no family of organic acids has excited so much interest amongst chemists, and been the subject of such numerous researches, as that represented by lactic acid. Its character, intermediate between the monobasic and bibasic acids, its close relations to the acetic and acrylic families, and the numerous important transformations which it undergoes, have all contributed to render this family an attractive subject for experimental inquiry and a fruitful source of theoretical speculation. These inquiries and hypotheses have contributed greatly to the elucidation of the habits of these acids, and still more to the general progress of organic chemistry. Nevertheless, there are two circumstances which have materially interfered with their complete success; these are, the comparatively small number of the known members of this series, and the absence of any synthetical proof of the nature of their constituent radicals. These obstacles to a more satisfactory conception of the internal architecture of the acids in question we have endeavoured to remove by the production, according to purely synthetical methods, of a number of new members of this series, a brief notice of which we have from time to time had the honour of submitting to the Royal Society,* and the more complete history of which we propose to develop in the following pages. Our general method for synthetically producing the acids of the lactic series depends upon the replacement of one of the atoms of dyad oxygen in oxalic acid, or rather in the ethereal salts of oxalic acid, by two semimolecules of monad alcohol radicals. Such a replacement at once transforms bibasic oxalic acid into a monobasic acid of the lactic series. The nature of this transformation, as well as

* Proceedings of the Royal Society, vol. xii, p. 396; vol. xiii, p. 140; vol. xiv, pp. 17, 79, 83, 191, 197, and 198.

the relations of oxalic acid to the lactic family, is clearly seen from the following comparison of the formulæ of oxalic acid and of its derivative, dimethoxalic acid:—



This substitution of alcohol-radicals for one atom of oxygen in oxalic acid can be readily effected by acting upon the ethereal salts of oxalic acid by the zinc-compounds of the alcohol-radicals.

I. *Action of Zincethyl upon Ethylic Oxalate.*

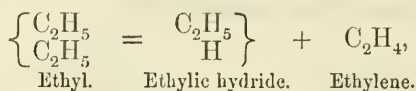
In this reaction ethylic oxalate† was mixed with rather more than its own volume of pure zincethyl; the temperature of the mixture gradually rose, and large quantities of gas were evolved consisting of about equal volumes of ethylic hydride and

* In this paper O = 16, C = 12, H = 1, Zn = 65, Ba = 137, Cu = 63·5; Ho = (OH) the monad radical hydroxyl or peroxide of hydrogen; Eto = (OC₂H₅) ethoxyl or peroxide of ethyl, &c.

† As large quantities of ethylic oxalate were required for this and the following reactions, it became a matter of importance to prepare this compound in the most economical manner. After trying the numerous methods which have been recommended, we found the following process to give the largest product:—

1,500 grammes of oxalic acid, thoroughly dried at 100° C., are placed, together with 1,000 grammes of absolute methylated spirit, in a capacious retort, which is then very slowly heated by an oil-bath to 100° C., at which temperature water begins to distil over; when the thermometer has risen to 105°, a steady stream of absolute methylated spirit is conducted to the bottom of the retort at the rate of about 80 grammes per hour, the temperature being allowed to rise very slowly to 125° 130° C., care being taken on the one hand that alcohol shall not distil over, in which case the temperature should be raised, and on the other that the heat be not so great as to cause the generation of gas. At this rate it requires about twelve hours to make the addition of 1,000 grammes of alcohol; after which the retort must be gradually heated to the boiling-point of ethylic oxalate, and the remainder of the distillate, which is the pure oxalic ether, collected apart. By fractional distillation the first portions afford a considerable additional quantity of the pure product besides ethylic formate. During the final operation, in consequence of the presence of some unconverted oxalic acid, a quantity of gas is always evolved; nevertheless, in frequently repeated operations, we have obtained an amount of pure ethylic oxalate equal in weight to the dried oxalic acid employed.

ethylene, and resulting from the decomposition of ethyl according to the following equation:—



For the attainment of the desired result of the reaction, it is best to prevent this secondary decomposition as much as possible. This we succeeded in doing by preventing the temperature from rising beyond 60° or 70° C., until the operation was considerably advanced. Afterwards it was necessary to heat to 100° C. to complete the reaction.

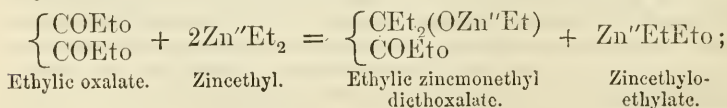
The mixture generally continues fluid, but assumes a light straw-colour and a thick oily consistency. On heating it to 130° C. in a retort, no distillate passes over. If, after cooling, its own volume of water be very gradually added, torrents of ethylic hydride are evolved, and, on subsequent distillation in a water-bath, weak alcohol containing an ethereal oil in solution passes over; a further quantity of the oil may be obtained by adding water to the residue in the retort, and continuing the distillation on a sand-bath. By repeated rectification the alcohol can be approximately separated from the water and oil, whilst the latter may then be removed by a separator.

The oily product so obtained was submitted to rectification, when its boiling point rapidly rose to 175°, at which temperature the whole of the remaining and very large proportion of the liquid distilled over.

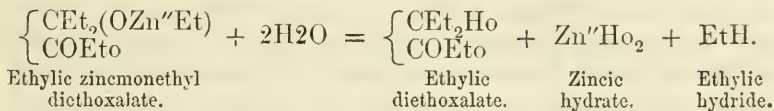
The analysis of this liquid yielded numbers agreeing with the formula—



We shall prove below that this body is the ethylic ether of an acid possessing the same composition as the leucic acid obtained by Strécker* in acting on leucine with nitrous acid. The two acids are probably isomeric; and we therefore prefer to call the one prepared synthetically *diethoxalic acid*, and the ether above analysed, *ethylic diethoxalate*. The formation of ethylic diethoxalate is explained in the following equations:—



* Ann. Ch. Pharm. lxxiii, 54.



The first of these equations expresses the action of zincethyl upon ethylic oxalate, by which ethylic zincmonethyl diethoxalate is formed.* The second shows the action of water upon this compound, by which the zincmonethyl (ZnC_2H_5) becomes replaced by hydrogen.† Although we have not been able to isolate the ethylic zincmonethyl diethoxalate from the other product of this decomposition, yet we have proved its existence by forming it synthetically, as described below.

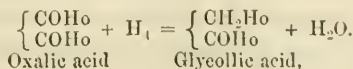
Ethylic diethoxalate is a colourless, transparent, and somewhat oily liquid, possessing a peculiar and penetrating ethereal odour, and a sharp taste. It is insoluble in water, but readily soluble in alcohol or ether. Its specific gravity is 1.9613 at $18^\circ.7$ C.; it boils at 175° C., and distils unchanged. Two determinations of the specific gravity of its vapour gave the numbers 5.241 and 5.23.

The formula $\text{C}_2 \left\{ \begin{array}{l} (\text{C}_2\text{H}_5)_2 \\ \text{OH} \\ \text{O} \\ \text{OC}_2\text{H}_5 \end{array} \right\}$ or $\left\{ \begin{array}{l} \text{CEt}_2\text{Ho} \\ \text{COEtO} \end{array} \right\} = 2$ vols. requires the number 5.528. We have remarked on this and other similar discrepancies below.

When zincethyl is added to ethylic diethoxalate previously cooled in a freezing mixture, each drop of the zinc compound, as it comes into contact with the ether, hisses like phosphoric anhydride when dropped into water. Torrents of ethylic hydride are evolved, and the mixture finally solidifies to a white tenacious mass, which melts on the application of heat, and does not distil below 100° C., at about which temperature a violent action sets in; a great quantity of gas is evolved, and

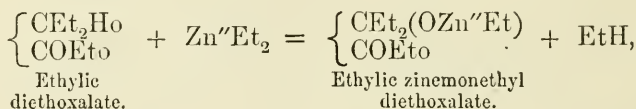
* This interpretation of the reaction was first proposed by Butlerow (Bull. Soc. Chimique, 1864, p. 116); and we have since confirmed it by the synthetical production of ethylic zincmonethyl diethoxalate, as described below.

† The final result of this reaction is exactly homologous with the production of glycollic acid by the action of nascent hydrogen upon oxalic acid, described by Schulze (Ann. Ch. Phys. lxxvii, 366),

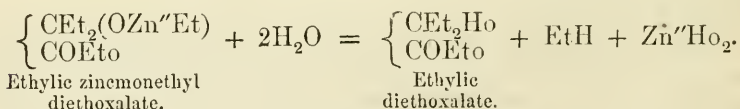


the residue solidifies to a pitch-like mass, which on treatment with water and subsequent distillation, yields about one-fourth of the ethylic diethoxalate employed. If the above-mentioned white mass, instead of being heated, be mixed with water, it effervesces strongly, zincic hydrate is formed, and pure ethylic diethoxalate separates, in quantity nearly equal to that originally employed.

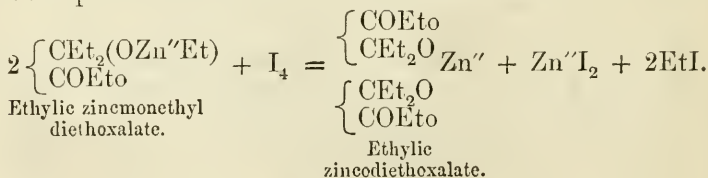
In a quantitative experiment 12.93 grms. of zincethyl were treated with ethylic diethoxalate, excess being avoided; 15.67 grms. of ethylic diethoxalate were required to saturate the above quantity of zincethyl, and the weight of ethylic hydride evolved, which was carefully determined, amounted to 3.08 grms. These numbers agree closely with those deduced from the following equation:—



Ethylic zincmonethyl diethoxalate is a colourless viscous solid, soluble in ether, but apparently incapable of crystallisation. It absorbs oxygen with avidity, and in contact with water effervesces strongly, reproducing ethylic diethoxalate, according to the following equation:—



Ethylic zincmonethyl diethoxalate combines energetically with iodine; an ethereal solution of the latter added to it is almost instantly decolorized, and a large quantity of ethylic iodide is produced.

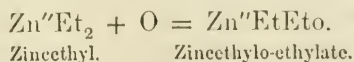


It was obviously impossible to collect in a state of purity the ethylic iodide thus set at liberty, without considerable loss:

but the quantity of the pure iodide actually obtained was 12 grms. The above equation requires 14·6 grms.

On the removal of ether and ethylic iodide, the mixture of ethylic zincodiethoxalate and zincic iodide forms a transparent gummy mass, easily soluble in ether, carbonic disulphide, or caoutchoucine, but totally incapable of crystallising from any of its solutions. All our attempts to separate these bodies have hitherto proved abortive; and it is by no means improbable that they are chemically combined.

The existence of monad organo-zinc radicals, such as zincmonethyl receives further support from the slow action of oxygen upon zincethyl, which clearly shows that there are two distinct stages in the process of oxidation. These stages have indeed already been indicated by one of us in describing the reactions of this body.* When a current of dry oxygen is made to pass through an ethereal solution of zincethyl, dense white fumes continue to fill the atmosphere of the vessel, until about one-half of the total quantity of oxygen necessary for the complete oxidation of the zincethyl has been taken up. Then the white fumes entirely cease, showing the absence of free zincethyl, and at the same moment the liquid, which up to that time had remained perfectly transparent, begins to deposit a copious white precipitate, and the latter continues to increase until the remaining half of the oxygen is absorbed. If the process of oxidation be arrested when the white fumes cease to be formed, the product effervesces violently when mixed with water, owing to the escape of ethylic hydride; but when the oxidation is completed, the white solid mass produced consists chiefly of zincethylate, and does not in the slightest degree effervesce in contact with water. The two stages of this reaction depend essentially upon the successive linking of the zinc with the two atoms of ethyl by means of dyad oxygen. The first stage of oxidation is expressed by the following equation:—



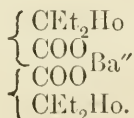
The zincethylo-ethylate thus formed is perfectly soluble in ether, and is instantly decomposed by water, according to the following equation:—

* Philosophical Transactions, 1855, p. 258.

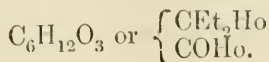
precipitated until the second stage is completed. Indeed, as shown in the memoir above referred to (Philosophical Transactions, 1855, p. 268), the oxidation, instead of stopping at the first stage, proceeds even somewhat further than the second, and the final product formed does not possess a composition in any degree approaching that which Butlerow asserts it to have. This is evident from the following numbers, and from the circumstance that it does not effervesce in the slightest degree when mixed with water:—

	Percentage composition according to Butlerow's formula, $\text{Zn}''\text{C}_3\text{H}_5\text{OC}_2\text{H}_5$.	Percentage composition according to mean of analyses.*
C	34.53	25.43
H	7.20	5.32
Zn.....	46.76	42.04
O	11.51	27.21
	<hr/> 100.00	<hr/> 100.00

When ethylic diethoxalate is treated with solution of baric hydrate, it gradually dissolves, even in the cold; on heating the solution in a water-bath, a liquid having the properties of alcohol distils off; and on separating the excess of baryta by carbonic anhydride and filtration, the solution yields on evaporation a crystallisable salt, consisting of baric diethoxalate,



Baric diethoxalate is very soluble, even in cold water; when its boiling solution is precipitated with excess of dilute sulphuric acid and the baric sulphate removed by filtration, ether readily extracts diethoxalic acid from the cooled filtrate. On evaporating the ethereal solution, the acid crystallises in splendid prisms, which, after drying *in vacuo*, gave results agreeing with the formula



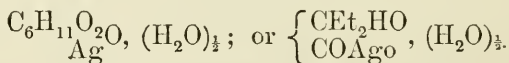
* Philosophical Transactions, 1855, p. 268.

Diethoxalic acid is very soluble in alcohol or ether, and somewhat less so in water. By the spontaneous evaporation of its aqueous solution, it crystallises in minute prismatic needles; but if a small quantity of dilute sulphuric acid be added to the solution, the crystals are deposited in magnificent anorthic prisms, which frequently attain a length of 1 inch, and a thickness of $\frac{1}{4}$ inch.

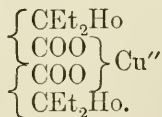
Diethoxalic acid is greasy to the touch, like stearic acid; it melts at $74^{\circ}5$ C., and slowly sublimes at the same temperature, but is decomposed before reaching its boiling point. It has a sour taste, reddens litmus strongly, and expels carbonic acid from carbonates. It forms an extensive series of salts, which are all soluble in water. In addition to the barium-salt described above, we have examined the silver, copper, and zinc salts.

Argentie diethoxalate is readily prepared by boiling an aqueous solution of the acid with excess of argentic carbonate. On filtration and evaporation *in vacuo*, the salt crystallises in brilliant needles, radiating from centres, standing up freely from the capsule, and containing half a molecule of water, which is not expelled at 100° C.

Submitted to analysis, this salt gave numbers indicating the formula



Cupric diethoxalate is obtained by mixing atomic proportions of baric diethoxalate with cupric sulphate, filtering, and evaporating to dryness. The salt does not crystallise, but dries down to a green gum-like mass, which becomes nearly white on being reduced to powder. Submitted to analysis, it yielded results agreeing with the formula



Zincic diethoxalate crystallises in nacreous scales, which are sparingly soluble in water and in alcohol. Two determinations of the solubility of this salt in water at 16° C. gave the following results:—

I. One part of the salt dissolved in 291 parts of water.

II. One part of the salt dissolved in 312 parts of water. Its solubility in boiling water is not much greater. Although so difficultly soluble in pure water, it dissolves very readily in a solution of zincic iodide.

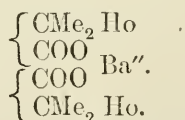
The method of producing ethylic diethoxalate above described involves the previous preparation of considerable quantities of zincethyl: but we have found that the process may be much simplified by generating the zincethyl during the reaction, which is effected by gently heating a mixture of granulated zinc, ethylic iodide, and ethylic oxalate for several hours. After long experience in the production of this and other homologous compounds described below, we have found the following process for the preparation of ethylic diethoxalate to give a maximum product.

600 grammes of a mixture consisting of one molecule of ethylic oxalate and two of ethylic iodide, were placed in a capacious flask with such a quantity of well-dried granulated zinc that the latter rose above the surface of the liquid. An inverted Liebig's condenser was attached to the flask. It is preferable to use zinc which has been employed in a previous operation, as it not only acts with greater rapidity, but also at a much lower temperature. The flask was immersed in water maintained at a temperature of about 30° C. After a period of time which varies in each operation, but is usually from twelve to twenty-four hours, an energetic action sets in, which must be checked by lowering the temperature of the water-bath. The reaction once commenced is usually completed in from twelve to eighteen hours, the temperature of the water-bath being maintained at about 30° C. until it is nearly concluded, when it may be raised to 100° C. The operation may be regarded as complete when the hot liquid assumes the consistency of honey, and solidifies to a more or less crystalline mass on cooling, although a considerable quantity of the mixed ethers is still unacted upon. Water being now gradually added until it equals three times the volume of the crystalline mass, with which it must be well mixed by agitation, a copious effervescence takes place; zincic oxalate and oxide are formed in abundance, whilst, on the application of the heat of an oil-bath, alcohol, accompanied by ethylic diethoxalate, distils over together with the ethylic iodide that has not been acted upon. This distillate is then treated in exactly the same manner as

that already described for the separation and purification of ethylic diethoxalate prepared by means of zincethyl. In the operation above mentioned with 600 grammes of the mixed ethylic iodide and oxalate, 86 grammes of pure ethylic diethoxalate were obtained, the theoretical amount being 105 grammes.

II. *Action of Zinc upon a Mixture of Methylic Iodide and Methylic Oxalate.*

Two molecules of methylic iodide were mixed with one molecule of methylic oxalate, and placed in contact with an excess of granulated zinc at 30° C. in a flask, as above described. At the conclusion of the reaction the liquid solidified to a crystalline mass, which, on distillation with water, yielded methylic alcohol possessing an ethereal odour, but from which no ether could be extracted. The residual magma in the flask, consisting of zincic iodide, zincic oxalate, and the zinc salt of a new acid, was separated from the metallic zinc by washing with water. It was then treated with an excess of baric hydrate, and boiled for a considerable time; carbonic anhydride was afterwards passed through the liquid until, on again boiling, the excess of baryta was completely removed. To the filtered solution recently precipitated argentic oxide was added until all iodine was removed. The solution separated from the argentic iodide was again submitted to a current of carbonic anhydride, boiled, and filtered. The resulting liquid, on being evaporated on the water-bath, yielded a salt crystallising in brilliant needles, and possessing the peculiar odour of fresh butter. This salt is very soluble in water and in alcohol, but nearly insoluble in ether, and perfectly neutral to test-papers. On being submitted to analysis, it gave numbers closely corresponding with the formula

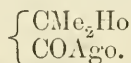


Dimethoxalic acid is obtained from its barium-salt by adding dilute sulphuric acid to a concentrated solution of the latter, and agitating with ether. On allowing the ether to evaporate

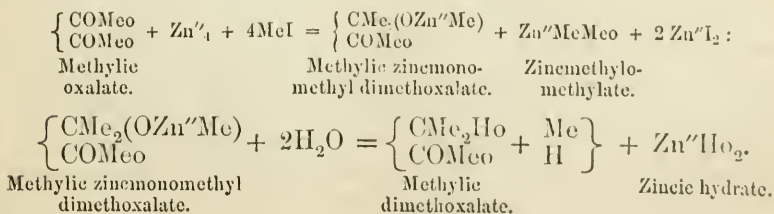
spontaneously, prismatic crystals of considerable size make their appearance. These yielded on combustion, results agreeing with the formula



Dimethoxalic acid is a white solid readily crystallising in beautiful prisms resembling oxalic acid. It melts at $75\cdot7^\circ\text{C}$., volatilizes slowly even at common temperatures, and readily sublims at 50°C ., being deposited on a cool surface in magnificent prisms. It boils at about 212°C ., and distils unchanged. Dimethoxalic acid reacts strongly acid, and unites with bases, forming a numerous class of salts, several of which are crystalline. In addition to the barium-salt above mentioned, we have examined the silver-salt, which is best formed by adding argentic oxide to the free acid, heating to boiling, and filtering, when the salt is deposited in starlike masses of nacreous scales as the solution cools. On analysis, this salt gave numbers closely corresponding with those calculated from the formula



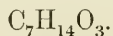
Attempts to produce ethylic dimethoxalate by digesting the free acid with absolute alcohol at a temperature of 160°C . proved abortive, traces only of the ether being apparently formed. Judging, however, from our subsequent success in obtaining ethylic dimethoxalate as described below, we believe that the methylic ether would probably be obtained by repeatedly agitating with ether the aqueous distillate obtained from the crude product of the original operation, methylic dimethoxalate being evidently, like ethylic dimethoxalate, miscible with water in all proportions. Assuming the formation of this ether, its production from the mutual action of zinc, methylic oxalate, and methylic iodide, followed by that of water, would be expressed in the following equations:—



Dimethoxalic acid exhibits the same composition as Staedeler's acetic acid, Wurtz's butylactic acid, and the oxybutyric acid obtained by Friedel and Machuca. The relations of these acids to each other will be discussed at the conclusion of this paper.

III. *Action of Zinc upon a Mixture of Ethylic Iodide and Methylic Oxalate.*

This reaction was performed in exactly the same manner as the last. On addition of water, the product yielded, on subsequent distillation, a considerable quantity of an ethereal body, which distilled over together with the ethylic iodide that had not been acted upon. The addition of water to the distillate effected an approximate separation of the ethereal from the alcoholic portion; the former was then decanted and distilled for the purpose of separating alcohol and ethylic iodide. When the temperature of ebullition rose to 100° C., the liquid left in the retort was placed over calcic chloride for twelve hours, after which it was again submitted to distillation. When its boiling point almost immediately rose to 165° C. (barom. 758.2 millims.), at which temperature the whole of the remaining liquid passed over. Submitted to analysis, this liquid yielded results closely corresponding to the formula

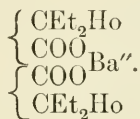


The decomposition of this ether by baryta described below, proves it to be the methylic ether of an acid of the same composition as diethoxalic acid, with which it also agrees in its fusing point. The composition of this ether may therefore be thus expressed,



Methylic Diethoxalate is a colourless, transparent, and tolerably mobile liquid, possessing a peculiar ethereal odour, only remotely resembling that of ethylic diethoxalate. It is very sparingly soluble in water, but readily soluble in alcohol or ether. Its specific gravity is .9896 at $16^{\circ}5$ C. It boils at 165° C., and distils unchanged. Its vapour-density was found by experiment to be 4.84. The above formula, corresponding to two volumes of vapour, requires the number 5.03.

Treated with caustic alkaline bases, this ether is readily decomposed even in the cold, yielding methylic alcohol and a diethoxalate of the base. A quantity of it was thus decomposed with solution of baryta, the excess of base being afterwards removed. It yielded on evaporation a crystalline mass very soluble in water, alcohol, or ether, and which on analysis gave results corresponding with those calculated from the formula of *baric diethoxalate*,



When this barium-salt in aqueous solution is decomposed with the exact amount of sulphuric acid necessary, the liquid filtered off from the baric sulphate, and evaporated *in vacuo*, the acid crystallises magnificently. Professor W. Hallows Miller of Cambridge, has kindly examined and measured these crystals for us with the following results:—

Anorthic:—

$$\begin{aligned} 100, 110 &= 66^\circ 2'; \\ 110, 010 &= 34^\circ 15'; 100, 001 = 76^\circ 40'; \\ 001, \bar{1}01 &= 29^\circ 4'; 010, 001 = 75^\circ 13'. \end{aligned}$$

Observed forms:—

$$100, 010, 001, 110, \bar{1}10, \bar{1}01, \bar{2}01.$$

	Angles.
010, 001	75 13
001, 0 $\bar{1}$ 0	104 47
100, 001	76 40
$\bar{1}$ 00, 001	103 20
100, $\bar{1}$ 01	105 44
$\bar{1}$ 00, $\bar{1}$ 01	74 16
100, 201	128 41
$\bar{1}$ 00, $\bar{2}$ 01	51 19
001, $\bar{1}$ 01	29 4
$\bar{1}$ 01, $\bar{2}$ 01	22 56
100, 010	100 17
$\bar{1}$ 00, 010	79 43

	Angles.	°	'
100, 110		66	2
010, 110		34	15
010, $\bar{1}10$		28	36
100, $\bar{1}10$		51	7
010, $\bar{1}01$		70	0
010, $\bar{2}01$		69	31
110, 001		68	19
110, $\bar{2}01$		91	52
$\bar{1}10$, 001		84	50
$\bar{1}10$, $\bar{1}01$		66	16
$\bar{1}10$, $\bar{2}01$		54	30

Combinations :—

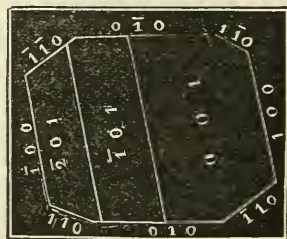
100, 010, 001, 110
 100, 010, 001, $\bar{1}01$
 100, 010, 001, 110, $\bar{1}01$
 100, 010, 001, 110, $\bar{1}10$
 100, 010, 001, 110, $\bar{1}01$, $\bar{2}01$
 100, 010, 001, 110, $\bar{1}01$, $\bar{1}10$
 100, 010, 001, 110, $\bar{1}01$, $\bar{1}10$, $\bar{2}01$.

Cleavage :—

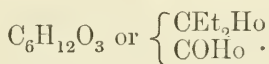
100, 010, very perfect and easily obtained.

The optic axes seen in air through the faces of the form 010 appear to make with one another an angle of about 71° . Denoting by α, β the extremities of radii of the sphere of projection drawn parallel to the directions of the optic axes seen in air through the faces of the form 010, the arcs joining α, β and the nearest poles of faces are approximately as follows :—

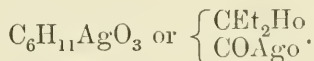
010, α	19	40
001, α	73	1
110, α	14	58
$\bar{1}00$, β	29	54
001, β	78	51
010, β	51	28



This acid is readily soluble in ether, alcohol, and water; it is greasy to the touch, and nearly inodorous. It sublimes readily at 50° C., and slowly even at common temperatures, a small quantity of the acid left on a watch-glass gradually disappearing, though in other respects it is permanent when exposed to the air. It fuses at 74°·5 C. Submitted to analysis it gave numbers agreeing with the formula



Argentio diethoxalate was made by adding argentic oxide to a hot solution of the acid. After filtration and evaporation *in vacuo*, it crystallises in brilliant silky fibres adhering closely to the capsule. These are anhydrous, and are scarcely discoloured by prolonged exposure to a temperature of 100° C. They yielded on analysis numbers closely corresponding with those calculated from the formula

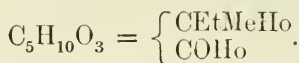


Although the diethoxalic acid obtained by the action of zincethyl upon methylic oxalate possesses the same molecular weight and fusing-point as that prepared by the action of zincethyl upon ethylic oxalate, yet the two acids do not appear to be identical. The silver-salt of the latter crystallises, as above described (page 36), in brilliant needles radiating from centres, standing freely up from the capsule, and containing half a molecule of water, which is not expelled at 100° C. This salt also further differs from that just described by being rapidly discoloured when exposed to the heat of a steam-bath. In a future communication we hope to be able to throw additional light upon this apparent isomerism.

IV. *Action of Zinc upon a Mixture of Ethylic Iodide, Methylic Iodide, and Ethylic Oxalate.*

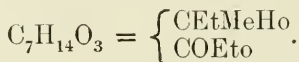
Having proved in the foregoing reactions the possibility of replacing one atom of oxygen in ethylic oxalate by two semi-molecules of either methyl or ethyl, we thought it desirable to ascertain whether the same replacement could be effected by a

semi-molecule of each of two different monad alcohol-radicals. We endeavoured to accomplish this by acting with zinc upon a mixture consisting of one molecule of ethylic oxalate and one molecule each of the methylic and ethylic iodides, by which we hoped to obtain an acid of the following composition:—

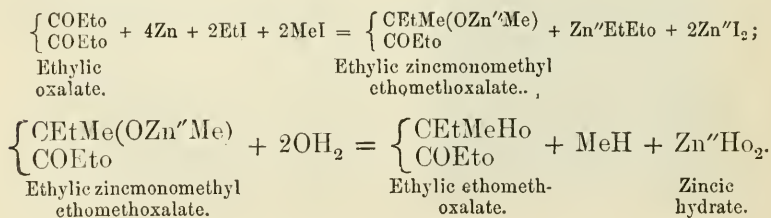


Experiment completely proved the practicability of this reaction; and its result even exceeded our expectations, since not only was the ether corresponding to the above acid formed with the greatest facility, but it was produced almost to the complete exclusion of the ethers of diethoxalic and diethoxalic acids.

200 grammes of ethylic oxalate were mixed with the proper atomic proportions of methylic iodide and ethylic iodide, and were digested with granulated zinc for several days at a temperature of from 35° to 40° C., until the supernatant liquid became oily, and solidified to a crystalline mass on cooling. Water being now added till effervescence ceased, the whole was submitted to distillation in an oil-bath. With the exception of a small quantity of the mixed ethylic and methylic iodides that had escaped decomposition, the distillate consisted of a homogenous liquid composed of water, ethylic and methylic alcohols and an ethereal body, which last was separated by repeated agitation with large volumes of ether and subsequent rectification. In this manner there was obtained a large quantity of a liquid which boiled constantly at $165^\circ\cdot5$ C., and yielded on analysis numbers very closely corresponding with the formula



The production of this ether is explained in the following equations:—

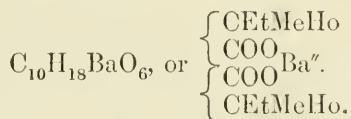


A not inconsiderable amount of the ether thus formed in this and in the analogous reactions described above, appears to be decomposed by the zincic hydrate; at all events an appreciable quantity of the zinc-salt of the derived acid is always obtained from the residue left after distillation of the ethereal product.

Ethylic ethomethoxalate, as we propose to name the new ether, is a colourless, transparent and mobile liquid, possessing a penetrating ethereal odour much resembling that of ethylic diethoxalate. It is very soluble in water, alcohol, and ether, and has a specific gravity of .9768 at 13° C. It boils at 165°·5 C.; and its vapour-density determined by experiment is 4·98, the theoretical number for a two-volume vapour of the above formula being 5·04.

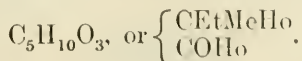
Ethylic ethomethoxalate is readily decomposed even by aqueous solutions of the alkalies and of baryta, yielding alcohol and a salt of the base. By this means baric ethomethoxalate was prepared. This salt crystallises from an aqueous solution as a beautiful radiated mass of silky lustre, very easily soluble in water.

Submitted to analysis, it gave results agreeing with the formula

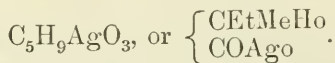


By exactly decomposing this salt with dilute sulphuric acid and evaporating the filtrate, first in a retort and afterwards in a vacuum, *ethomethoxalic acid* was obtained as a splendid white crystalline mass, fusing at 63° C., subliming readily at 100° C., and condensing in magnificent star-like groups upon a cold surface. It boils, with decomposition, at 190° C. Ethomethoxalic acid is very readily soluble in ether, alcohol, or water; small fragments of it thrown upon water rotate like camphor whilst dissolving. These solutions react powerfully acid, and readily decompose carbonates.

The analysis of this acid gave results corresponding with the formula



Argentio ethomethoxalate was prepared by treating the free acid dissolved in water with argentic carbonate. The salt crystallises in splendid mammillated masses half an inch in diameter, which are tolerably soluble in water. It gave on analysis numbers agreeing with the formula



V. *Action of Zinc upon a Mixture of Amylic Iodide and Ethylic Oxalate.*

When a mixture of equivalent proportions of ethylic oxalate and amylic iodide is digested with granulated zinc at 70°C ., the zinc is gradually dissolved, while much amylic hydride and amylene are given off. The mixture finally assumes a viscous or semisolid condition, and when treated with water produces a further quantity of amylic hydride, which distils off at a gentle heat. On the subsequent application of a higher temperature, water accompanied by amylic alcohol, amylic iodide, and an ethereal liquid distil over, the three latter forming a mixture, the separation of which into its component parts presents rather formidable difficulties. After drying with calcic chloride, the oily mixture begins to boil at about 132°C .; the product first passing over consists principally of amylic alcohol mixed with amylic iodide. Afterwards the thermometer rapidly rises to 200°C ., between which temperature and 205°C . a considerable section of the remaining liquid, which we will call A, passes over. There then occurs a further rapid rise of temperature until the thermometer remains stationary between 222° and 226°C . The section collected between these points we will call B. Finally, the temperature rises to 260° to 264° , between which points the remaining liquid (C) passes over. By repeated fractional distillation, the larger portion of the section A was obtained at the nearly fixed boiling point of 203°C . This liquid was submitted to analysis and yielded numbers coinciding nearly with the formula



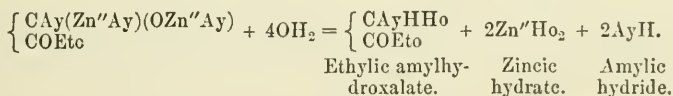
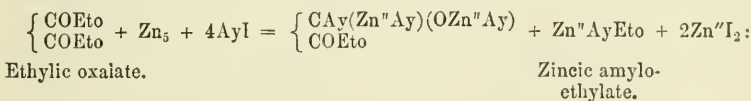
which, interpreted by further results detailed below, resolves itself into



The ethereal body with the lowest boiling point produced in this reaction is therefore *ethylic amylhydroxalate*, or ethylic oxalate in which one atom of oxygen is replaced by one semi-molecule of amyl and one of hydrogen. This body also stands in very close relation to ethylic lactate; for if the semi-molecule of methyl in ethylic lactate were replaced by amyl, ethylic amylhydroxalate would be produced,



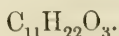
The two stages in the production of ethylic amylhydroxalate are explained in the following equations:—



We have not attempted to give a name to the body from which ethylic amylhydroxalate is directly produced by the action of water, as shown in the last of the foregoing equations. The resources of chemical nomenclature, already too severely taxed, would scarcely be able to elaborate a constitutional name for this body, which consists of ethylic oxalate, wherein an atom of oxygen is replaced half by amyl and half by zincmonamyl, whilst a second semi-molecule of zincmonamyl is substituted for a semi-molecule of ethyl.

Ethylic amylhydroxalate is a somewhat oily, transparent, and slightly straw-coloured liquid, of specific gravity 0.9449 at 13° C., possessing a pleasant aromatic odour and burning taste. It boils at 203° C.; and its vapour-density, determined by experiment, is 5.47, the above formula requiring 6.0. To this discrepancy we shall refer again presently.

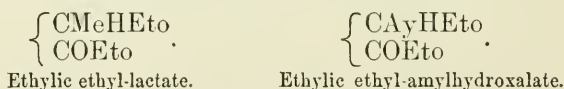
Section B of the oily liquid, after careful rectification, gave a product boiling at 224—225°, which yielded on analysis results agreeing with the formula



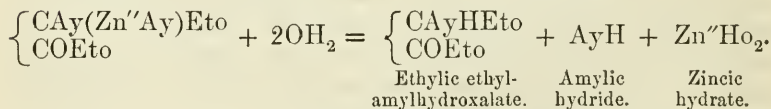
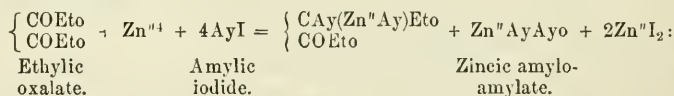
The above formula might be interpreted as that of *ethylic amyloxoalate*, the constitutional formula of which would be



We were at first inclined to regard this as the actual constitution of the new ether, believing it to be possible that ethylic oxalate and amylic iodide mutually decomposed each other, producing a mixture of amylic and ethylic oxalates with the amylic and ethylic iodides; an analogous decomposition of mixed ethereal salts of oxygen acids has been recently noticed; but the test of experiment obliged us to abandon this view of the reaction. We found, it is true, a remarkable depression of temperature, amounting to 9°·3 C. on mixing one molecule of ethylic oxalate with one of amylic iodide; but on submitting the mixture to distillation, the thermometer rose to the boiling point of amylic iodide (147°) before ebullition commenced, thus showing that none of the much more volatile ethylic iodide had been formed. No transfer of radicals therefore takes place when ethylic oxalate is heated with amylic iodide; and consequently no zincethyl can be formed when this mixture is acted on by zinc. We therefore prefer to view the ether now under consideration as ethylic ethyl-amyllhydroxalate, analogous in constitution to Wurtz's ethylic ethyl-lactate.*



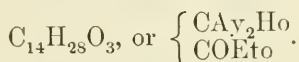
On this view the following equations represent the formation of the ether:—



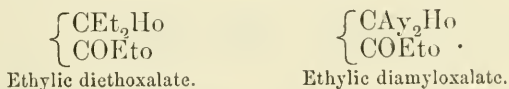
* It deserves to be mentioned that the identity of boiling point between this ether and its isomer amylic diethoxalate described below does not favour this view, since a comparison of the boiling points of ethylic ethyllactate with that of ethylic ethoxalate and methylic diethoxalate, its isomers, shows that the substitution of ethyl for the hydrogen of hydroxyl is attended with a depression of the boiling point equal to 8°·5 C., the percentage composition of the compound remaining constant.

Ethylic ethyl-amylhydroxalate is a straw-coloured oily liquid, possessing an aromatic but somewhat amylic odour and a burning taste. Its specific gravity was found to be .9399 at 13° C. It boils between 224° and 225° C. A determination of the specific gravity of its vapour by Gay-Lussac's method gave the number 6.29, whilst the above formula requires 6.92.

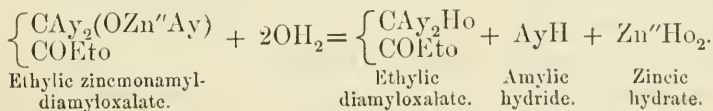
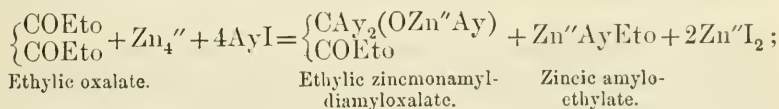
Section C of the oily product, boiling about 262° C., was next submitted to investigation. It gave on analysis results agreeing approximately with the formula



The body is therefore *ethylic diamyloxalate*, the normal homologue of ethylic diethoxalate, as is seen from the following comparison:—



The production of ethylic diamyloxalate is explained by the following equations:—



Ethylic diamyloxalate closely resembles the two foregoing ethers in its appearance and properties. It is, however, a thicker oil, and flows less readily, and has the lowest specific gravity of any ether belonging to this series, its density at 13° C. being only .9137.

The following comparison of the specific gravities of all the ethers of this series shows that they generally increase inversely as their atomic weights:—

	Formula.	Sp. gr.	Temp.	Observer.
Ethylic lactate. .	C ₅ H ₁₀ O ₃	1.042	13	Wurtz & Friedel.
Ethylic dimeth- oxalate . . }	C ₆ H ₁₂ O ₃	0.9931	13	F. & D.

	Formula.	Sp. gr.	Temp.	Observer.
Ethylic ethyl-lactate ..	$C_7 H_{14} O_3$	0.9203	0	Wurtz.
Ethylic etho-methoxalate ..	$C_7 H_{14} O_3$	0.9768	13	F. & D.
Methylic dieth-oxalate ..	$C_7 H_{14} O_3$	0.9896	16.5	"
Ethylic diethox-alate ..	$C_8 H_{16} O_3$	0.9613	18.7	"
Ethylic amyldro-xalate ..	$C_9 H_{18} O_3$	0.9449	13	"
Amylic diethox-alate ..	$C_{11} H_{22} O_3$	0.9322	13	"
Ethylic ethyl-amyldro-xalate ..	$C_{11} H_{22} O_3$	0.9399	13	"
Ethylic diamyl-oxalate ..	$C_{14} H_{28} O_3$	0.9137	13	"

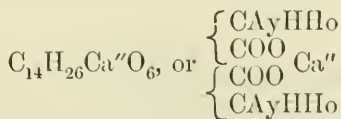
Ethylic diamyloxalate boils at about 262° , and distils with little or no change. A determination of the specific gravity of its vapour gave the following numbers:—

Weight of ethylic diamyloxalate	..	2043	grm.
Observed volume of vapour	..	56.78	cup. centims.
Temperature of bath	..	273	$^\circ$ C.
Height of barometer	..	769	millims.
Difference of heights of mercury inside and outside tube	..	70	millims.
Height of spermaceti column reduced to millims. of mercury..	..	14	millims.

From these data the specific gravity 5.9 was deduced, whilst the above formula requires 8.4. The investigation of these ethers has revealed a tendency to dissociation, increasing with the weight of the semi-molecules replacing the atom of oxygen in ethylic oxalate. Thus, beginning with ethylic lactate, which has the normal vapour-density, we find a gradual divergence culminating in ethylic diamyloxalate, as seen in the following series of numbers:—

Name.	Formula.	Vapour-densities.		Observer.
		Calculated.	Found.	
Ethylic lactate..	$C_5 H_{10} O_3$	4.07	4.14	Wurtz & Friedel.
Ethylic dimeth- oxalate ..	$C_6 H_{12} O_3$	4.56	4.67	F. & D.
Ethylic ethyl- lactate ..				
Ethylic etho- methoxalate ..	$C_7 H_{14} O_3$	5.03	5.052	Wurtz.
Ethylic dieth- oxalate ..				
Ethylic diethox- alate ..	$C_8 H_{16} O_3$	5.528	5.24	F. & D.
Ethylic amyly- droxalate ..				
Ethylic ethyl- amylyhydrox- alate ..	$C_9 H_{18} O_3$	6.01	5.47	"
Ethylic ethyl- amylyhydrox- alate ..				
Amylic diethox- alate ..	$C_{11} H_{22} O_3$	6.92	6.29	"
Ethylic diamyl- oxalate ..				
Ethylic diamyl- oxalate ..	$C_{14} H_{28} O_3$	8.4	5.9	"

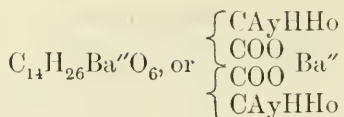
We have likewise prepared the acids corresponding to the three ethers above mentioned. The first is obtained by decomposing ethylic amylyhydroxalate with baryta, treating the solution of the barium-salt thus obtained with excess of sulphuric acid, and then dissolving out the organic acid with ether. On evaporating the ethereal solution, the acid remains as a thick oil which does not crystallise after several days' exposure over sulphuric acid *in vacuo*. The calcium-salt forms a white crystalline mass soluble in water. Submitted to analysis, .2102 gm. gave .0877 gm. calcic sulphate, corresponding to 12.27 per cent. of calcium, the formula



requiring 12.12 per cent.

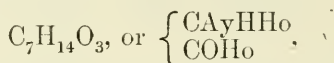
The barium-salt closely resembles that of calcium.

.2476 gm. gave on analysis .1334 gm. baric sulphate, corresponding to 31.68 per cent. of barium. The formula

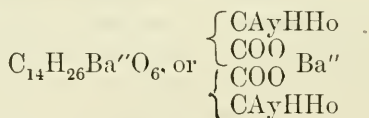


requires 32·08 per cent. of barium.

We have also obtained a beautifully crystalline acid of the same composition as the above, from its zinc-salt contained in the residue remaining after the distillation of the three ethers above described. *Amylhydroxalic acid* prepared from this zinc-salt is but sparingly soluble in water, from which, however, it crystallises in magnificent nacreous scales which fuse at 60°·5 C., but afterwards remain liquid for some time even at ordinary temperatures; they are very unctuous to the touch, and readily soluble in alcohol and ether. On analysis this acid gave results agreeing well with those calculated from the formula



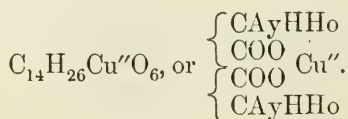
The barium-salt of this acid crystallises in large and beautiful nacreous scales like paraffin, tolerably soluble in water; ·3765 gm. gave on analysis ·2027 gm. baric sulphate, corresponding to 31·66 per cent. of barium. The formula



requires 32·08 per cent. of barium.

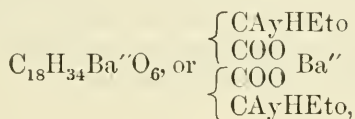
A copper-salt was also prepared. It is deposited from its aqueous solution in minute light-blue scales, very sparingly soluble in water.

Submitted to analysis, ·2341 gm. of it gave numbers agreeing closely with the formula



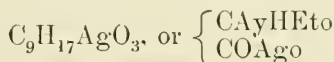
The acid of the second ether, *ethyl-amylhydroxalic acid*, is prepared by the decomposition of ethylic ethyl-amylhydroxalate with alcoholic potash. The acid is afterwards liberated by the

addition of sulphuric acid in excess, and may then be dissolved out of the mixture by ether. On the evaporation of the latter, the acid remains as a thick oil gradually solidifying to a crystalline mass, which, however, did not appear to be in a fit state for the determination of its fusing point. The barium- and silver-salts of this acid were prepared. They are both soluble in water; 1.331 grm. of baric ethyl-amylhydroxalate gave, on decomposition with sulphuric acid, .0660 grm. baric sulphate, corresponding to 29.15 per cent. of barium, the formula



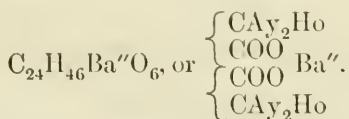
requiring 28.41 per cent. of barium.

1.891 grm. of argentic ethyl-amylhydroxalate gave on ignition .0722 grm. metallic silver, representing 38.18 per cent. The formula



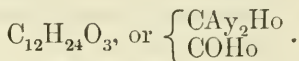
requires 38.43 per cent. of silver.

The acid of the third ether (*diamyloxalic acid*) is best prepared by decomposing the ether with boiling baryta-water. After removing the excess of baryta in the usual manner, baric diamyloxalate crystallises on evaporation in minute elastic needles, which, when dry, have the appearance of wool. It is moderately soluble in hot water, but sparingly so in cold. Two determinations of barium in this salt gave results agreeing with the formula



If baric diamyloxalate be dissolved in hot dilute alcohol and excess of sulphuric acid be added, the liquid after filtration contains diamyloxalic acid in solution. On heating upon a water-bath, the alcohol gradually evaporates and diamyloxalic acid crystallises in the hot solution as a beautiful network of brilliant silky fibres, which after being well washed in cold

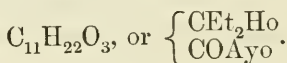
water, and dried at 100°, yielded on analysis numbers agreeing well with the formula



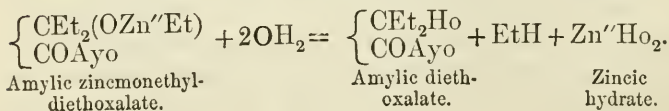
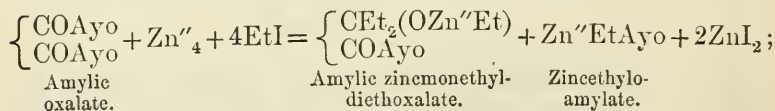
Diamyloxalic acid presents the appearance of colourless satiny fibres, which are insoluble in water, but soluble in alcohol or ether. This acid is remarkable for its high melting point, 122° C., in which respect it surpasses any of the acids of this series. Its melting point is very sharply defined, and it solidifies immediately on a very slight reduction of temperature. Heated more strongly, it sublimes and condenses on a cold surface in white crystalline flakes like snow.

VI. *Action of Zinc upon a Mixture of Ethylic Iodide and Amylic Oxalate.*

Equivalent proportions of amylic oxalate and ethylic iodide were digested at 50° to 60° with excess of granulated zinc for several days. The reaction proceeded with extreme sluggishness, and was not completed before the expiration of a week. The mass being then mixed with water and submitted to distillation, an oily liquid passed over, which on rectification was ultimately resolved into amylic alcohol and an ethereal liquid. Submitted to analysis the latter yielded numbers agreeing closely with those calculated from the formula of amylic diethoxalate,

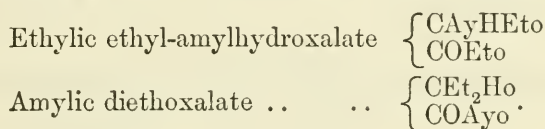


The two consecutive reactions by which amylic diethoxalate is produced are expressed in the following equations:—



Amylic diethoxalate is a colourless, transparent, and slightly oily liquid, possessing a fragrant odour of a somewhat amylic character. It is insoluble in water, but miscible in all proportions with alcohol and ether. Its specific gravity is $\cdot 93227$ at 13° C. It boils constantly at 225° C. Its observed vapour-density is $6\cdot 74$, the above formula requiring $6\cdot 97$.

Amylic diethoxalate is isomeric with ethylic ethyl-amylhydroxalate described above. The nature of this isomerism is seen at a glance from the following constitutional formulæ of the two bodies:—



The specific gravities, in the liquid form, and the boiling points of amylic diethoxalate and its isomer ethylic ethyl-amylhydroxalate, are almost absolutely identical, viz.

	Boiling point.	Specific gravity.
Ethylic ethyl-amylhydroxalate	224° — 225° C.	$\cdot 9399$ at 13° C.
Amylic diethoxalate	225° C.	$\cdot 9322$ at 13° C.

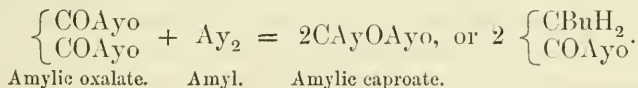
They are, however, at once distinguished by the products of their decomposition with alkalis, ethylic ethyl-amylhydroxalate giving ethylic alcohol and a salt of ethyl-amylhydroxalic acid, whilst amylic diethoxalate yields amylic alcohol and a salt of diethoxalic acid.

VII. *Action of Zinc upon a Mixture of Amylic Iodide and Amylic Oxalate.*

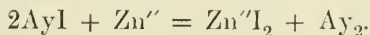
When equivalent proportions of amylic iodide and amylic oxalate are gently heated in contact with zinc, a brisk reaction soon sets in. After evolving much amylic hydride and amylene, the whole solidifies to a gum-like mass, which, on distillation with water, yields an oily liquid resembling that obtained when ethylic oxalate is employed. We have every reason to believe that the same series of ethers as those described under No. V. are here produced, with the difference that they are amylic instead of ethylic ethers. This difference

caproate is not known; but ethylic caproate boils, according to Fehling, at 162° C.; consequently the boiling-point of amylic caproate ought to be, according to Kopp's law, 216° C., a number which lies between the points observed in the ether under consideration.

It is thus evident that the three variations in the action of zincamylide upon an oxalic ether, described above as giving rise to amylhydroxalic acid, ethyl-amylhydroxalic acid, and diamyloxalic acid, do not exhaust the fertility of this reaction; and the production of caproic acid, as above described, shows that the action of these substances upon each other is susceptible of yet a fourth modification, in which the molecule of amylic oxalate appears to divide into its two constituent semi-molecules of amyloxatyl (COAyo), which then unite with amyl to form amylic caproate.



The source of the amyl in this reaction is not difficult to discover; for, as above stated, torrents of the usual products of its transformations (amylic hydride and amylene) were evolved during the operation; in fact it was obvious that no inconsiderable portions of the zinc and amylic iodide were occupied in the formation of zincic iodide and amyl, a considerable proportion of the latter being, as usual, transformed, at the moment of separation, into amylic hydride and amylene:



Meeting with this reaction, as we have done, only at the close of the above investigation, we have not been able to ascertain whether or not it is one of general occurrence. It is true that we have not observed the formation of the fatty ethers in any of the foregoing reactions in which zinc and the iodides of the radicals were employed; but the comparatively low boiling-points of these ethers might easily have led to their being overlooked. We consider, however, this reaction of so much importance, that we shall at once endeavour to ascertain whether or not it occurs in the other homologous cases, giving rise to acetic ether in the case of

methylic iodide, and to propionic ether where ethylic iodide is employed.

We have already stated that the constitution of the acids of the lactic series has been the subject of fruitful controversy amongst chemists. In this discussion, widely different opinions have been advanced: some have assigned to lactic acid the formula ($C_6H_{12}O_6$), and attributed to it a bibasic character; some have reduced this formula to $C_3H_6O_3$, still retaining for the acid the same degree of basicity; whilst others, again, have regarded it as monobasic, and assigned to it the lower formula. This controversy respecting the constitution of an acid so intimately related to several of the most important families of organic compounds, has been the incentive to numerous and highly important researches, which have thrown valuable light, not merely upon the structure of the lactic series itself, but also upon that of organic families allied to this series.

Amongst the experimental investigations which have contributed to the elucidation of this subject, we beg leave to refer to those of Wurtz,* Ulrich,† Strecker,‡ Brüning,§ Perkin and Duppa.¶ Again, Wurtz, Perkin, Kekulé, and especially Kolbe, have, by their acute theoretical speculations, most ably supplemented direct investigation.

Unfortunately these researches and discussions were, to a great extent, limited to two members of this series, viz., lactic and glycollic acid, and this circumstance necessarily furnished a comparatively small basis upon which to build purely theoretical speculations. We are, therefore, not without hope that, with the addition of the numerous members of this series described in the foregoing pages, and with the light thrown upon them by their synthetical production, we have reached a new stage in the inquiry, whence a more extensive prospect may be obtained.

Before proceeding to take a survey of the new field thus opened up, it is necessary first to call special attention to a negative or chlorous organic radical intimately connected with the compounds above described.

* Comptes Rendus, vol. lii, p. 1067.

‡ Ann. Chem. Pharm. vol. xci, p. 352.

† Ann. Chem. Pharm. vol. cix, p. 271.

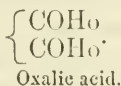
§ Ibid. vol. civ, p. 191.

¶ Ibid. vol. cviii, p. 113.

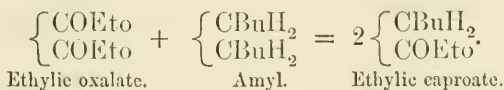
The Radical Oxatyl.

An inspection of the above and following formulæ for acids of the lactic series shows that, through all the changes of the lactic acid type, giving rise to the various species of acids mentioned below, the group COHo remains unaltered. We have also shown that the same group maintains its individuality unimpaired throughout the acetic and acrylic series of acids; in fact it is the presence of this group which impresses upon an organic compound the acid character. We believe, therefore, that its claims to be considered a compound radical are at least equal to those of any other group of elements to which that term has been applied.

We propose for this radical the name *oxatyl**—a word recalling at the same time its acidifying power, and its connexion with oxalic acid, which is the isolated molecule of this radical,



We have, in fact, experimentally proved above, that when ethylic oxalate is acted upon by nascent amyl, it is converted into ethylic caproate,



Oxatyl is closely related to cyanogen, the two radicals passing into each other in a host of reactions; hence the production of cyanides from the ammonium salts of the fatty acids on the one hand, and the synthesis of acids from certain cyanogen compounds on the other—a reaction which was first pointed out by Kolbe and Frankland,† and has of late yielded such magnificent results in the hands of Maxwell Simpson‡ and of Kolbe and Hugo Müller.§

* *Oxatyl* would obviously be the most appropriate name for this radical, had it not already been applied to the two compounds CO and C_2O_2 . Whilst this paper is passing through the press, we find that the radical oxatyl has already been fully recognized by Butlerow.

† Memoirs of Chem. Soc. vol. iii (1847), p. 386.

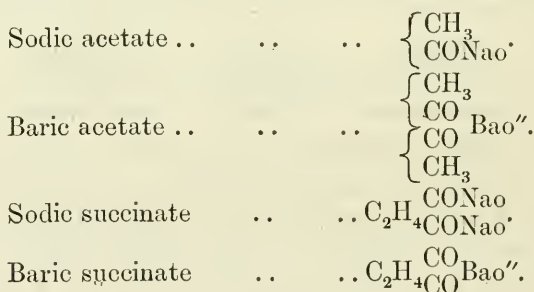
‡ Philosophical Transactions, 1861, p. 61; and Journ. Chem. Soc. vol. xviii, p. 331.

§ Journ. Chem. Soc., vol. xvii, p. 109.

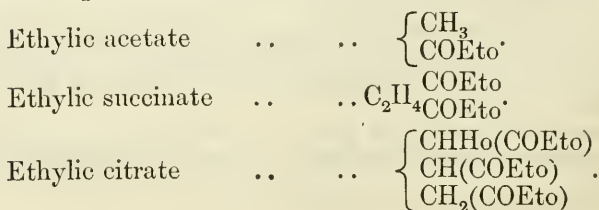


The researches of these chemists prove that the introduction of cyanogen into an organic compound, and its subsequent transformation into oxatyl, converts that compound into an acid, or, if already an acid, increases its basicity by unity for each semi-molecule of oxatyl so developed, this result being apparently quite independent of the position of the oxatyl in the molecule.

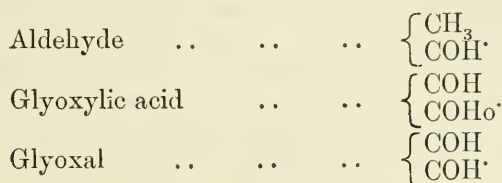
The semi-molecule of oxatyl, as the above molecular formula shows, may be regarded as methyl (CH_3) in which two atoms of hydrogen have been replaced by one of oxygen, and the third by hydroxyl (Ho). The individualizing of this group confers upon the formulæ of most of the great families of organic compounds a simplicity hitherto unattainable without ignoring their atomic constitution. The passage from one organic family to another thus becomes a mere substitution of the hydroxyl contained in oxatyl by other radicals, either simple or compound. When, for instance, it is replaced by the peroxide of a metal, the acid of which the oxatyl is a constituent becomes converted into a salt, thus :



With the hydroxyl replaced by methoxyl, ethoxyl, &c., an ethereal salt is produced, as



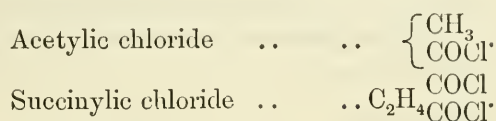
When the hydroxyl is replaced by hydrogen, an aldehyde or an aldehydoid acid is the result. Thus



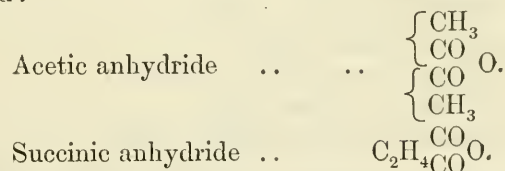
Again, if a basylous monad radical take the place of the hydroxyl, a ketone is formed,



Further, if chlorine, bromine, &c., replace the hydroxyl, a haloid compound of the so-called "acid radical" is the result:



Again, if the hydroxyl be replaced by oxygen, an anhydride is formed:



And, finally, if replaced by amidogen, an amide or amido-acid results:



It may be objected that the group of elements which is thus invested with radical functions, lacks one of the fundamental characteristics of a radical by its proneness to change; but the characteristic of persistency is exhibited by the commonly

received radicals in a very varied degree; and even methyl itself, which certainly possesses it in the most marked manner, readily permits of its hydrogen being replaced by chlorine or bromine on the one hand, and by sodium on the other.

All compound radicals are purely conventional groupings of elements, intended to simplify the expression of chemical change; and in this respect we believe the group oxatyl, entering as it does into the constitution of nearly every organic acid, has as valid a claim to a distinct name as the most universally recognized radicals. Its admission renders possible the following very simple expression of the law governing the basicity of nearly all organic acids:—

An organic acid containing n semi-molecules of oxatyl is n-basic.

Classification of the Acids of the Lactic Series.

We propose classifying all acids of the lactic series at present known, or which could be obtained by obvious processes, into the following eight divisions:—

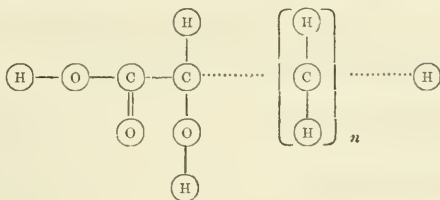
1. Normal Acids.
2. Etheric Normal Acids.
3. Secondary Acids.
4. Etheric Secondary Acids.
5. Normal Olefine Acids.
6. Etheric Normal Olefine Acids.
7. Secondary Olefine Acids.
8. Etheric Secondary Olefine Acids.

1st. *Normal Acids.*—A normal acid of the lactic series may be defined as one in which an atom of carbon is united with oxatyl, hydroxyl, and at least one atom of hydrogen. The general formula of these acids is therefore



In this formula $\overset{+}{\text{R}}$ may be either hydrogen or any monad alcohol radical; and the number of acids possessing the same atomic weight, and belonging to this division, is determined by the number of isomeric modifications of which the radical $\overset{+}{\text{R}}$ is susceptible. Thus, of the acids containing two, three, or four

atoms of carbon, there can be only one of each belonging to this division, because these acids cannot contain an alcohol radical higher in the series than ethyl, which is not susceptible of isomeric modification; but a normal acid containing propyl can have one isomer in this division, the two acids containing respectively propyl (CEtH_2) and isopropyl (CMe_2H). For acids of this division containing normal alcohol radicals only, the following general graphic formula may be given:—

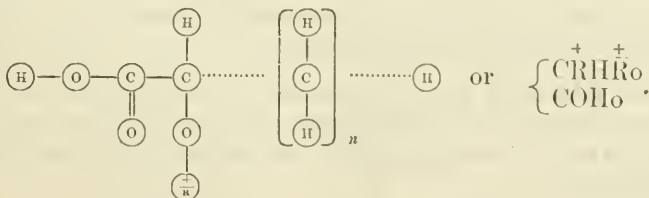


In the case of glycollic acid $n = 0$.

The following are the acids at present known belonging to this division*:

Glycollic acid	$\begin{cases} \text{CH}_2\text{Ho} \\ \text{COHo} \end{cases}$
Lactic acid	$\begin{cases} \text{CMeHHo} \\ \text{COHo} \end{cases}$
Oxybutyric acid	$\begin{cases} \text{CEtHHo} \\ \text{COHo} \end{cases}$
Leucic acid	$\begin{cases} \text{CBuHHo} \\ \text{COHo} \end{cases}$

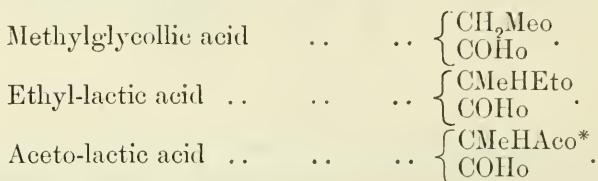
2nd. *Etheric Normal Acids*.—An etheric normal acid of the lactic series is constituted like a normal acid, but contains a monad organic radical, chlorous or basylous, in the place of the hydrogen of the *non-oxytylic* hydroxyl. The following is, therefore, the general formula of these acids: in the graphic formula n , as before, may = 0.



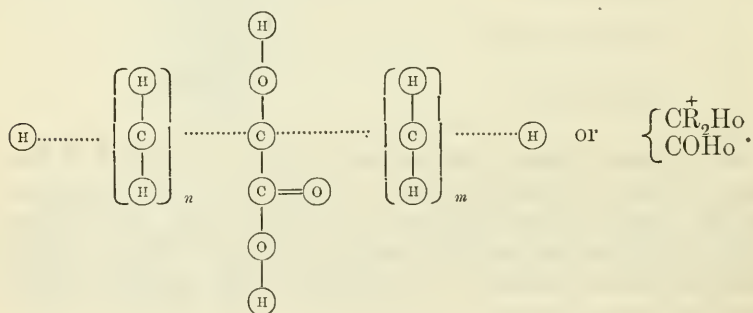
* Since the above was written Fittig has produced valerolactic acid, the rational formula of which is doubtless $\begin{cases} \text{CPrHHo} \\ \text{COHo} \end{cases}$.—April 29th, 1866.

The number of possible isomers belonging to this division is very great; for, in addition to those of which the normal acids containing $\overset{+}{R}$ of the same value are susceptible, a host of others must result from the complementary variation of $\overset{+}{R}$ and $\overset{+}{\bar{R}}$. The lowest member of the division, methylglycollic acid (isomeric with lactic acid), is the only one incapable of isomeric modification.

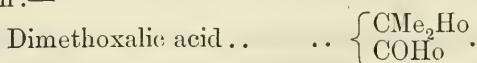
The following examples will serve to illustrate the constitution of the acids belonging to this division:—



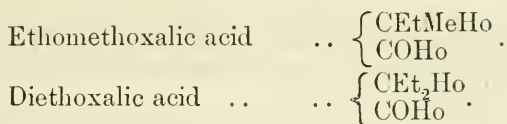
3rd. *Secondary Acids*.—A secondary acid of the lactic series is one in which an atom of carbon is united with oxatyl, hydroxyl, and *two semi-molecules* of an alcohol radical. The general formula of these acids is



In the graphic expression, the values of n and m may differ, but both are positive integers, and neither may = 0. In the symbolic formula $\overset{+}{R}$ must be a monad alcohol radical. All the known members of this division are described in the foregoing pages. The following examples will serve to illustrate their constitution:—

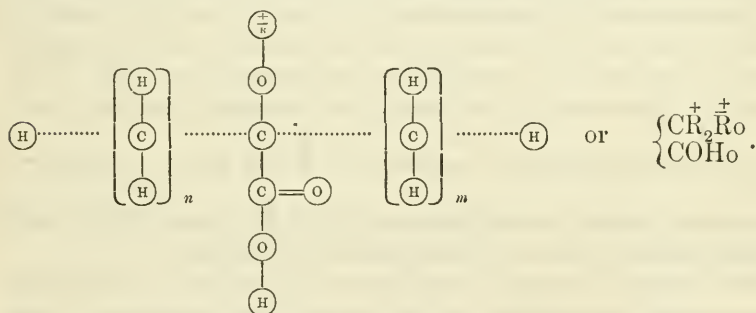


* Aco = peroxide of acetyl, $\text{C}_2\text{H}_3\text{O}_2$.



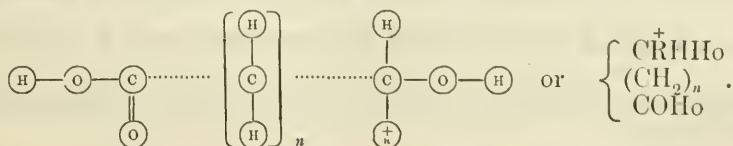
The number of acids possessing the same molecular weight, and belonging to this division, is determined, first, by the complementary variation of the two alcohol radicals, and, secondly, by the number of possible isomers of these radicals. The two lowest terms of the series are alone incapable of isomeric modification by either of the causes mentioned.

4th. *Etheric Secondary Acids*.—These acids stand in the same relation to the secondary as the etheric normal to the normal acids; they consequently contain a monad organic radical in the place of the hydrogen of the non-oxatylic hydroxyl. The following is therefore the general formula of these acids:—



We have obtained acids belonging to this division which we hope to describe in an early communication.

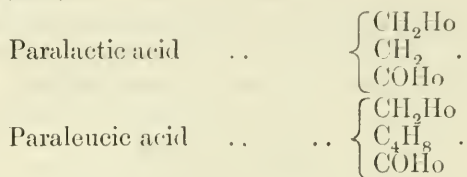
5th. *Normal Olefine Acids*.—A normal olefine acid belonging to the lactic series is one in which the atom of carbon united with oxatyl is *not* combined with hydroxyl, and in which the atom of carbon united with hydroxyl is combined with not less than one atom of hydrogen. The following are the general graphic and symbolic formulæ of the acids belonging to this division:—



In both these formulæ n must be a positive integer and can-

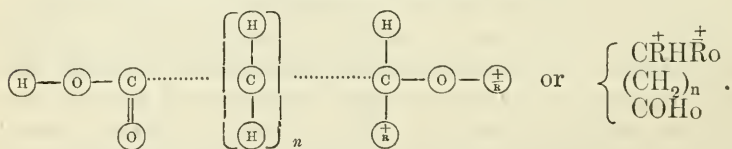
not = 0, but $\overset{+}{R}$ may be either hydrogen or a monad alcohol radical. The olefines of these acids may belong to either the ethylene or ethylidene series.

The following are the only acids at present known belonging to this division :—



We give the name paraleucic acid to the acid obtained by Lippmann* in acting with phosgene gas upon amylene. This body has not yet been completely investigated; Lippmann regards it as identical with leucic acid, but as it is produced by a reaction exactly homologous with that by which paralactic acid is formed, we believe it will be found to differ slightly from leucic acid, as paralactic does from lactic acid. The number of isomers in this division will obviously depend, first, upon the complementary variations of $\overset{+}{R}$ and $(\text{CH}_2)_n$; secondly, upon the isomeric modifications of which $\overset{+}{R}$ is susceptible; and thirdly, upon the isomeric modifications of $(\text{CH}_2)_n$.

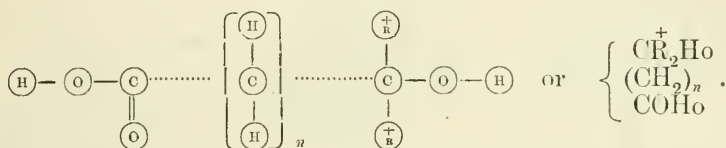
6th. *Etheric Normal Olefine Acids*.—These acids differ from the normal olefine acids only in having the hydrogen of the non-oxatylic hydroxyl replaced by an organic radical positive or negative; therefore their general formula is



As in the fifth division, n must be a positive integer and cannot = 0, whilst $\overset{+}{R}$ may be either hydrogen or a monad alcohol radical; but $\overset{+}{R}$ must be a monad compound radical, either acid or alcoholic.

* Ann. Ch. Pharm. cxxix. 81.

7th. *Secondary Olefine Acids*.—A secondary olefine acid of this series is one in which the atom of carbon united with oxatyl is *not* combined with hydroxyl, and in which the atom of carbon united with hydroxyl is also combined with two monad alcohol radicals, as shown in the following formulæ:—



In both of these formulæ n must be a positive integer and cannot = 0, and R^\dagger must be a monad alcohol radical.

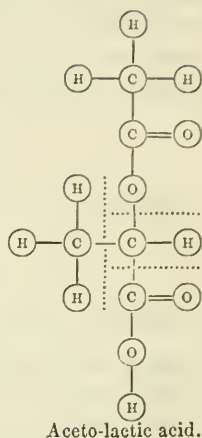
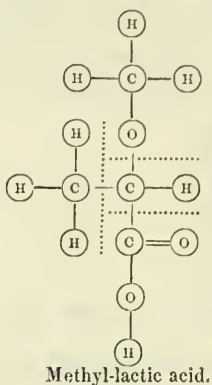
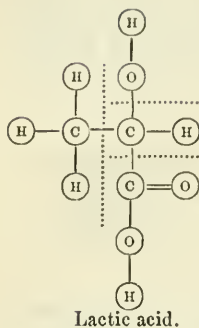
8th. *Etheric Secondary Olefine Acids*.—These acids are related to the secondary olefine acids in the same way as the sixth division to the fifth. No member of the seventh or eighth division has yet been formed.

Isomerism in the Lactic Series.

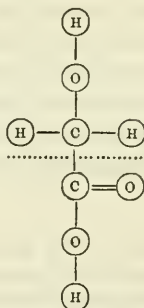
The members of the lactic series may be defined as acids containing one semi-molecule of oxatyl, the fourth bond of the carbon of which is united with the carbon of a basylous group containing one semi-molecule, and one only, of hydroxyl, or of the peroxide of a radical, either alcoholic or acid. The following examples, expressed in the graphic notation of Crum Brown,* will serve to illustrate this definition.

* Edinburgh Phil. Trans. for 1864, p. 707. It is much to be desired that chemists should employ these graphic formulæ in all cases where they wish to express the mode in which they suppose the elements of a chemical compound to be combined. It is often extremely difficult to trace in symbolic formulæ the exact meaning which an author attaches to the grouping of letters; in graphic formulæ no such difficulty can arise; and we therefore think that the use of these formulæ, where constitutional expressions are intended, will greatly tend to clearness and precision. It is scarcely necessary to repeat Crum Brown's remark, that such formulæ are not meant to indicate the physical, but merely the chemical position of the atoms. For the purpose of rendering the graphic more easy of comparison with symbolic formulæ, we have sometimes dissected the former into their constituent radicals by dotted lines, as above. This dissection, whilst assisting the eye in reading the formulæ, cannot fail to suggest the, for the most part, purely conventional character of such radicals.

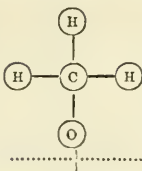
Acids of the Lactic Series.



The synthetical study of the acids of this series affords an insight into numerous and interesting cases of isomerism, which have hitherto received, at best, but a very imperfect explanation. Commencing with the lowest member of the series, we have for glycollic acid the formula—



An inspection of this formula shows that glycollic acid admits of no isomeric modification, except with a total change of type, *unless a different value be assigned to the individual bonds of an atom of carbon.* The part of the formula below the dotted line represents oxatyl, which, as we have already shown, cannot be altered without sacrificing the acid character of the compound; there remains, therefore, only the part of the formula above the dotted line, which admits of the following modification :—

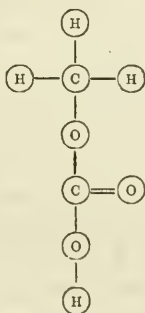


The acid represented by the formula so modified no longer comes within our definition of the lactic series. It is carbomethylic acid, and differs essentially from glycollic acid and the lactic series in general, inasmuch as the carbon of its chlorous radical, oxatyl, is linked to the carbon of the basylous radical by oxygen.*

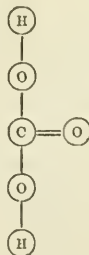
There being no decisive evidence that homolactic acid differs from glycollic acid, experiment and theory both agree in asserting that the formula $C_2H_4O_3$ represents only one acid in the lactic series.

Proceeding now one step higher in this series, we have in the formula of lactic acid an expression capable of the following three variations without quitting the lactic type:—

* Bearing this constitution of carbomethylic acid in mind, we have only to go one step further in order to perceive the constitution of carbonic acid itself, and the anomalous basicity of that acid; for if, in the above graphic formula, for carbomethylic acid we replace the methyl by hydrogen, we have

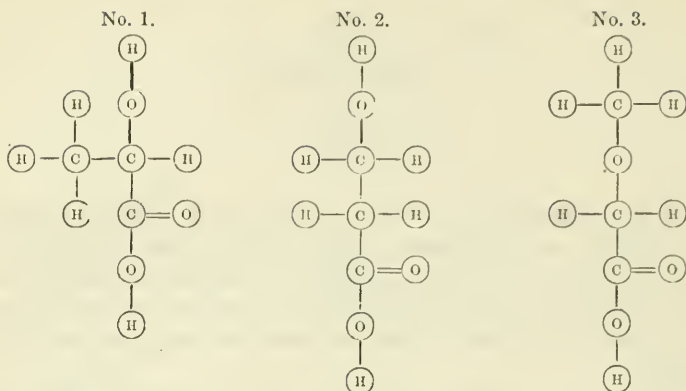


Carbomethylic acid.

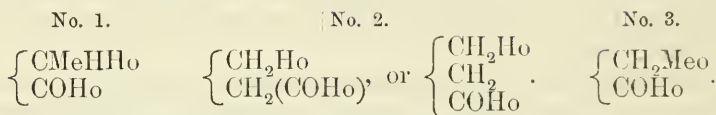


Carbonic acid.

It is thus evident that our radical oxatyl, when united with hydroxyl, has sufficient chlorous power to produce a feebly bibasic acid, but inasmuch as carbonic acid is not included in the category of organic acids, it forms no exception to the law above enunciated.



Or expressed symbolically,

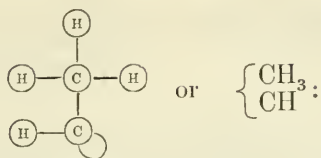


All the acids represented by the above formulæ are known. The first expresses the constitution of lactic acid, which belongs to the normal division $\left(\begin{cases} \text{CR}^+\text{HHo} \\ \text{COHo} \end{cases} \right)$ of the series described

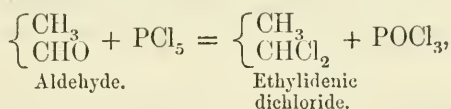
at page 62; the second shows the atomic arrangement of paralactic acid, whilst the third represents methyl-glycolic acid. The proof that the first two of these acids are so constituted is afforded by the beautiful synthetic processes for their production devised by Wislicenus* and Lippmann.† The first of these chemists has shown, namely, that ethylidene cyanhydrate is converted by ebullition with potash into a salt of lactic acid, whilst ethylene cyanhydrate is transformed under similar circumstances into paralactic acid. Lippmann has also shown that by the action of phosgene gas upon ethylene, paralactic acid is produced. Now the formation of ethylidene, or rather of its compounds, scarcely leaves a doubt that this body if isolated, would have the following atomic constitution:—

* Ann. der Ch. und Pharm. Bd. cxxviii. S. 1.

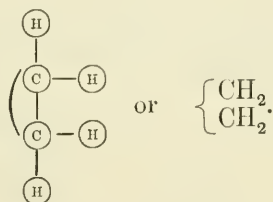
† Ibid. Bd. cxxix. S. 81. Crum Brown has already pointed out this relation between lactic and paralactic acids, as well as the formula of ethylene given below.—Edinburgh Phil. Trans. for 1864, p. 712.



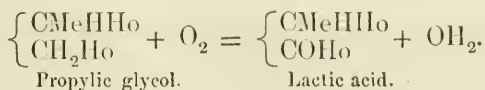
it would consist of a semi-molecule of methyl united with an atom of carbon, two of whose bonds satisfy each other. Thus the formation of ethylenic dichloride from aldehyde and phosphoric chloride takes place as follows:—



the oxygen in the aldehyde being simply replaced by chlorine. There now only remains one possible formula for ethylene, viz. :—

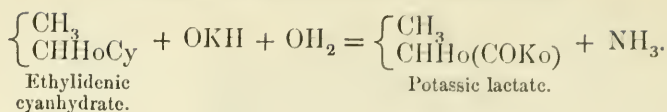


Such, then, being the constitution of ethylenic and ethylene, it follows that the former ought to give rise to an acid of the constitution shown in formula No. 1, whilst ethylene should produce an acid agreeing with formula No. 2. The acids actually produced from these sources are lactic and paralactic acids; hence we believe No. 1 to be the constitutional formula of lactic acid, and No. 2 that of paralactic acid, a conclusion which harmonizes perfectly with all the reactions in which the production of these acids can be traced. Thus in the formation of lactic acid by the oxidation of propylic glycol,* we have



Again, the production of this acid from ethylenic cyanhydrate,

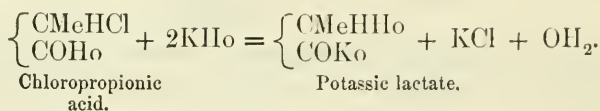
* Wurtz, Ann. der Chem. und Pharm. Bd. cv. S. 205.



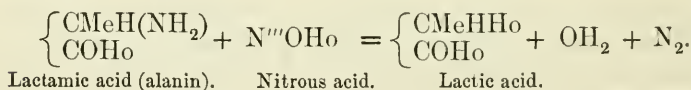
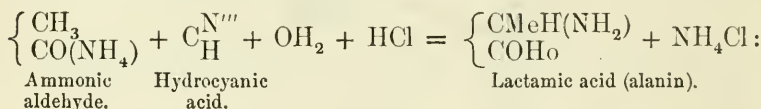
The formula given for potassic lactate in this equation is only apparently different in type from that previously used for lactic acid, since



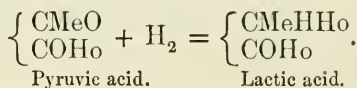
In Ulrich's* interesting reaction, by which chloropropionic acid is transformed into lactic acid, we have the following change:—



The production of lactamic acid (alanin), and that of lactic acid from the latter by the action of nitrous acid, are also clearly confirmatory of the above view.



Not the least interesting reaction illustrative of the constitution of lactic acid, is the formation of this acid by the action of nascent hydrogen upon pyruvic acid, recently described by Wislicenus.†

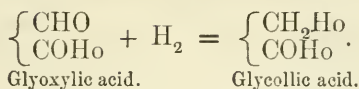


By an analogous reaction, glyoxylic acid, which we regard as the next lower homologue of pyruvic acid, has been transformed by Debus‡ into glycollic acid.

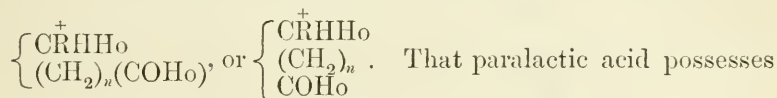
* Ann. Chem. Pharm. cix. 271.

† Ibid. cxxvi. 225.

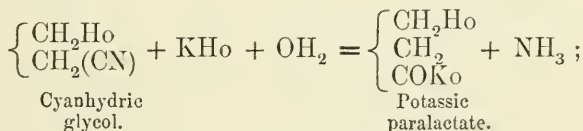
‡ Ibid. cxxvii. 145.



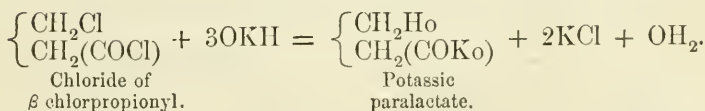
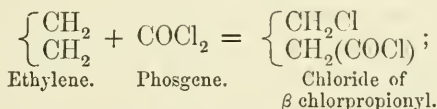
In a similar manner it can be demonstrated that the above formula No. 2 expresses the constitution of paralactic acid, which belongs to the fifth or olefine division of these acids,



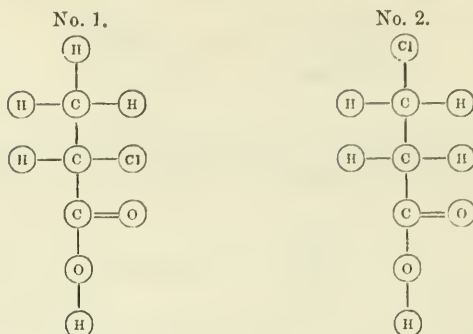
this constitution is proved, first, by its production from cyanhydric glycol,



and secondly, by its formation from phosgene gas and ethylene,

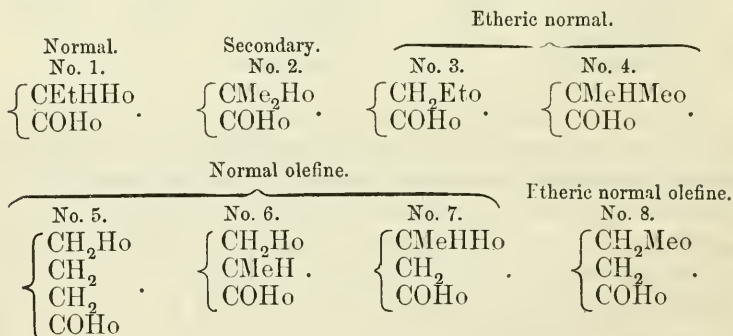


By the action of water upon the chloride of β chlorpropionyl, a body of the composition of chloropropionic acid results; but inasmuch as this body yields paralactic acid by ebullition with potash, whilst chloropropionic acid gives under the same circumstances lactic acid, it follows that the former chloro-acid must be isomeric, and not identical, with the latter. Now, although the formula of propionic acid does not admit of any isomer, yet that of chloropropionic acid does, as is seen in the following graphic formulæ:—



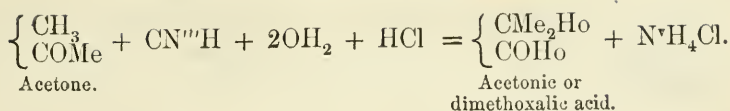
A comparison of these formulæ with those of lactic and paralactic acids (page 70) shows at a glance that No. 1 is the chloropropionic acid which yields lactic acid, whilst No. 2 is isochloropropionic acid, which, by the substitution of its chlorine by hydroxyl, must yield paralactic acid. By the action of nascent hydrogen, both isomeric chlorides will obviously produce the same propionic acid.

The cause of the isomerism of methyl-glycollic acid (No. 3, page 70) is so obvious as to require no further explanation. Proceeding to the next higher stage in the series, such is the rapid increase of isomerism, that we now encounter no less than eight possible isomers, all within the lactic family.



Of these acids, Nos. 1, 2, and 3 are known. No. 1 is oxybutyric acid; No. 2 is dimethoxalic acid, which is probably identical with Stadeler's acetic acid.* On this assumption, the formation of the latter by the action of hydrocyanic and hydrochloric acids upon acetone is easily intelligible.

* Ann. Ch. Pharm. cxi, 320. These acids have since been proved to be identical.

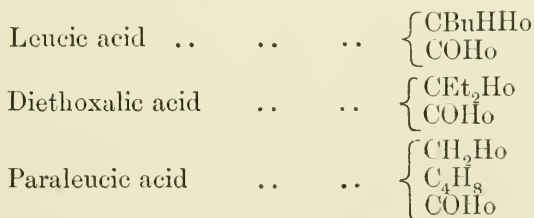


The properties of acetonic acid and its salts, as described by Stadeler, agree well with those which we have observed in dimethoxalic acid and its compounds: both acids evolve an odour of acetone on being heated with potassic hydrate, and are decomposed without blackening by concentrated sulphuric acid, with evolution of much gas.

The third of the above formulæ is obviously that of Heintz's ethyl-glycollic acid.* The origin of Wurtz's butylactic acid, which was prepared by an analytical process, does not permit of any safe conclusion being drawn as to its constitution.

Of the possible acids containing five atoms of carbon, only one (the ethomethoxalic acid described above) is known.†

Of acids containing six atoms of carbon three are known, to which we assign the following formulæ?—



The above formula for leucic acid is founded upon Limpricht's‡ interesting reaction for the synthetical production of this acid from valeric aldehyde and hydrocyanic acid.

Kolbe has shown that valeric acid contains butyl; consequently valeraldehyde has the constitution expressed by the

formula $\begin{Bmatrix} \text{Bu} \\ \text{COH} \end{Bmatrix}$, and Limpricht's reaction may therefore be

explained by the following equation,

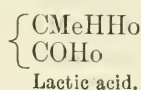
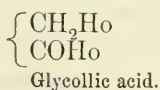
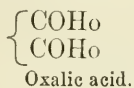
* Pogg Ann. cix. 331.

† Valerolactic acid, $\left(\begin{Bmatrix} \text{CPrHHo} \\ \text{COH}_o \end{Bmatrix} \right)$, just discovered by Fittig, forms a second.

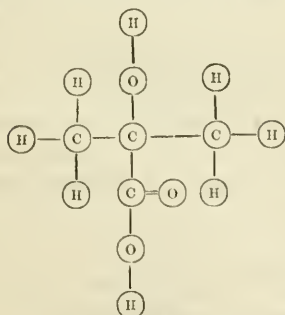
Its isomerism with ethomethoxalic acid is proved by its melting-point, which is 80°C., whilst ethomethoxalic acid fuses at 63°C. —April 29, 1866.

‡ Ann. Ch. Pharm. xciv, 243.

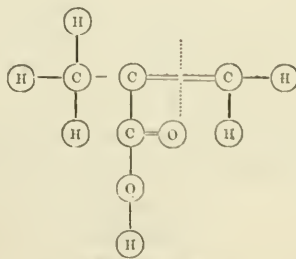
which are thus regarded as derived from oxalic acid, by the replacement of one atom of oxygen in the latter, either by hydrogen alone, as in glycollic acid, or by one atom of hydrogen and one semi-molecule of a monad alcohol radical :—



Hitherto we have advanced only synthetical evidence of this constitution; but the question presents itself, if the radicals indicated by our hypothesis really exist in these acids, can they not be again disentangled from the complex molecule, either in the condition in which they entered it, or at all events, in the form of well recognized derivatives? Such analytical evidence, although possessing far less weight than synthetical, may still be of service as corroborative testimony. We will therefore show how such a proximate analysis of these acids can be accomplished, and, for this purpose, we will first endeavour to demonstrate that if in a chain of carbon atoms any two be united by two bonds of each, the remaining atoms being united to each other by one bond only, the chain is more liable to rupture at the point of double junction than at any other. We have shown how in dimethoxalic acid a weak link of this kind can be developed;* for if dimethoxalic ether be treated with phosphorous chloride, it is transformed into ethylic methacrylate, the acid of which contains two atoms of carbon in the condition just indicated. The nature of this transformation and the link in the chain which is thus weakened are shown in the following graphic formulæ:—



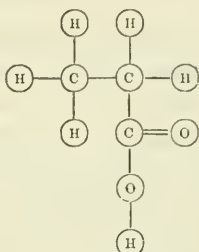
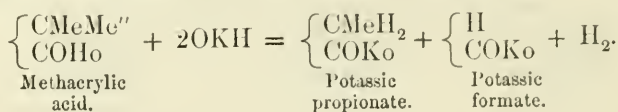
Dimethoxalic acid.



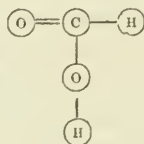
Methacrylic acid.

* Journ. Chem. Soc. vol. xviii p. 141.

If methacrylic acid be now heated with potash, the acid molecule breaks up at the place indicated by the dotted line, with the production of propionic and formic acids :—

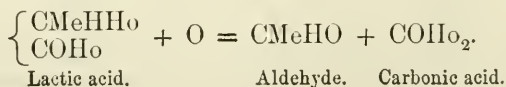


Propionic acid.



Formic acid.

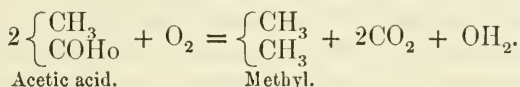
Thus one of the atoms of methyl originally introduced into oxalic acid is now extracted in the shape of its well-known derivative, formic acid. We have proved by synthesis that propionic acid is methacetic acid, $\left\{ \begin{array}{l} \text{CMeH}_2 \\ \text{COH} \end{array} \right.$; but it still remains to extract this second atom of methyl from it. For this purpose we might transform the propionic acid into chloropropionic acid, and the latter into ethylic lactate, by well-known processes, when, by repeating the reactions with phosphorous chloride and caustic potash above described, the second atom of methyl, like the first, ought to be eliminated as formic acid; but unfortunately the reaction with terchloride of phosphorus, although so easy with a secondary acid, fails when applied to a normal acid of the lactic series, and we are therefore driven to seek other means of obtaining the end in view. It is, however, only necessary to avail ourselves of the beautiful reactions of Kolbe* in order to extract the remaining atom of methyl in its integral form. Thus if the lactic acid, derived as above described, be submitted to the action of electrolytic oxygen, it is transformed into carbonic acid and aldehyde,



* Ann. Chem. Pharm. cxiii, 244.

It will be observed that one of the atoms of oxatyl in the original oxalic acid ($\begin{Bmatrix} \text{COHo} \\ \text{COHo} \end{Bmatrix}$) is here eliminated as the well-known derivative, carbonic acid.

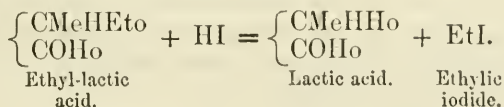
The aldehyde thus obtained, which contains the methyl sought for, must now be oxidized to acetic acid; and it then only remains to resort once more to electrolytic oxygen to liberate the methyl, together with the remaining atom of oxatyl, originally present in the oxalic acid,



We tabulate below the materials used in the synthesis of dimethoxalic acid side by side with the products obtained by the analysis of that acid:—

Materials for Synthesis.		Results of Analysis.	
I.	II.	I.	II.
$\begin{Bmatrix} \text{COHo} \\ \text{COHo} \end{Bmatrix}$	$\begin{Bmatrix} \text{CH}_3 \\ \text{CH}_3 \end{Bmatrix}$	2COHo_2	CH_3 COHHo
Oxalic acid.	Methyl.	Carbonic acid.	Methyl. Formic acid.

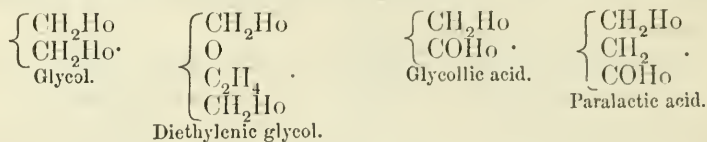
In like manner the radicals contained in the other acids belonging to the normal and secondary divisions of the lactic series can be extracted, whilst it has already been proved by Butlerow* that etheric normal acids, when treated with concentrated solution of hydriodic acid, yield up, as iodide, the alcohol radical which in these acids is linked to carbon by oxygen; thus in the case of ethyl-lactic acid,



The olefine acids are as yet too little known to allow of their constitution being thus analytically investigated. These acids do not derive from oxalic acid by substitution alone, but by simultaneous addition of an olefine. They may, in fact, be regarded as standing somewhat in the same relation to the

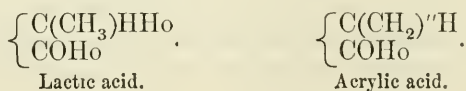
* Ann. Chem. Pharm. cxviii, 326.

normal acids as the polyethylenic glycols occupy with regard to the normal glycols, as seen from the following comparison :—



We beg to append the following summary of conclusions to which our investigations have conducted us :—

1. All acids of the lactic series are essentially monobasic.
2. These acids are of four species, viz., normal, secondary, normal olefine, and secondary olefine acids; and each of these species has its own etheric series of acids, in which the hydrogen of the hydroxyl contained in the positive or basylous constituent of the acid is replaced by a compound organic radical, either positive or negative.
3. The normal acids are derived from oxalic acid by the replacement of one atom of oxygen, either by two atoms of hydrogen, or by one atom of hydrogen and one semi-molecule of an alcohol radical.
4. The secondary acids are derived from oxalic acid by the replacement of one atom of oxygen by two semi-molecules of monad alcohol radicals.
5. The olefine acids are derived from oxalic acid by a like substitution of two monad positive radicals for one atom of oxygen, with the insertion of an olefine or dyad radical (C_nH_{2n}) between the two semi-molecules of oxetyl.
6. The acids of the lactic series stand to the acids of the acetic series in the very simple relation first pointed out by Kolbe, viz., that by the replacement, by hydrogen, of the hydroxyl, ethoxyl, &c., contained in the positive radical of an acid of the lactic series, that acid becomes converted into a member of the acetic series.
7. The acids of the lactic series stand in an almost equally simple relation to those of the acrylic series, as is seen on comparing the following formulæ :—



VI.—*On the connection between the Mechanical Qualities of Malleable Iron and Steel, and the amount of Phosphorus they contain.*

By B. H. PAUL, Ph.D.

IT has been customary to consider the presence of very small amounts of phosphorus or sulphur in malleable iron, and more especially in steel, as being among the circumstances most prejudicial to the quality of the metal. This opinion is generally expressed in chemical text-books and metallurgical treatises; but there appears to be much uncertainty as to the actual amounts of these substances which are sufficient to cause deterioration of the quality of malleable iron or steel. Phosphorus is considered to render the metal weak, and what is technically termed "cold short." As regards steel, it has recently been stated by an eminent metallurgist* to be a fact, at least as well established and as generally accepted as any relating to metallurgy, that much less than about 0·3 per cent. of phosphorus produces a decided and injurious effect.

There is probably little reason to question the general acceptance of the opinion, that a very small amount of phosphorus exercises a prejudicial influence on the quality of steel, but at the same time there does not appear to be any definite or satisfactory evidence that this opinion is well founded, nor any sufficient proof that the observed inferiority, in certain cases, of the steel or malleable iron made from phosphuretted pig iron, is really due to the presence of phosphorus in the metal; still less is there any reasonable explanation to be met with either as to the way in which phosphorus affects the qualities of the metal, or as to the state in which it may exist. In fact, the view held in regard to this subject, though based to some extent on experience of a limited nature, is unsupported by any scientific evidence, and it rests mainly on the fact that certain celebrated varieties of malleable iron and steel of very high quality are known to be either free from phosphorus, or to contain only infinitesimal amounts of that substance, rarely exceeding $\frac{1}{20000}$ in malleable iron, and $\frac{1}{30000}$ in steel.

The opinion that the presence of phosphorus affects injuriously the qualities of steel and malleable iron, has lately

* Dr. Percy, "Times," 7th January, 1869.

received considerable support from the experience gained in the application of the Bessemer method of converting pig-iron, for it has been found to be a coincidence, which so far as I am aware is invariable, that pig-iron containing as much as 0.1 per cent. of phosphorus is unsuitable for working by that method. As there is no elimination of phosphorus effected by the Bessemer method, this amount of phosphorus has consequently been regarded as the maximum proportion which steel can contain without its quality being deteriorated. This conclusion appears to be a generalization much wider than is justified by the facts observed, for it is still questionable whether the coincidence between the presence of a certain amount of phosphorus and the inferiority of the steel, may not be purely accidental, and whether the inferiority of steel made from phosphuretted pig-iron may not be due to some other circumstance than the presence of phosphorus. The probability of this being the case occurred to me some years ago, when I had occasion to give special attention to this subject, and quite recently an opportunity has offered itself for testing the sufficiency of the received opinion. Some considerable surprise has been excited by the publication of an analysis by Dr. Miller, of a sample of so-called "steel iron," which gave the proportion of phosphorus as amounting to 0.292 per cent., while the results obtained by Mr. Kirkaldy in testing a large number of samples of this metal, showed that it gave indications of very excellent quality in regard to tensile strength and ductility. These results, taken together with the amount of phosphorus indicated by Dr. Miller's analysis, as being present in the metal, appeared to be so inconsistent with the general opinion as to the influence of phosphorus in rendering malleable iron weak and "cold short," that I thought a further examination of other samples of this metal would be desirable; for if phosphorus were really the cause of weakness, and if it were that substance which rendered iron "cold short," it seemed to me that the tensile strength of the metal was precisely the character that should be most prejudicially influenced by the presence of such an amount of phosphorus. If, therefore, the analysis of several bars of this "steel iron," which had been tested as to their tensile strength, and gave results showing that this was considerable, should at the same time indicate the presence of phosphorus to any great extent, it appeared to me that there

would at least be some ground for questioning the opinion hitherto held as to the influence of that substance on the quality of iron, and some evidence that, in regard to the amount of phosphorus which might exist in malleable iron and steel without affecting its quality, something yet remained to be learnt either as to the state in which the phosphorus existed, or as to the conditions by which any prejudicial effects of its presence might be counteracted.

With this object I obtained, through the kindness of Mr. Noyes, portions of several bars of "steel iron," produced from various kinds of pig-iron, all of which bars had been tested by Mr. Kirkaldy, as to their tensile strength and other mechanical qualities. These samples were examined for phosphorus quantitatively with the following results:—

No. of bar.	Tensile strength in pounds per square inch sectional area.	Permanent extension of bar, per cent.	Kind of pig-iron produced from.	Amount of phosphorus per cent.
1,090	51,671	25·5	{ Clay Lane, No. 4 pig.* Stanton forge pig, BBB.†	·206
1,091	51,181	24·5	{ Clay Lane, No. 4 pig.* Stanton forge pig, BBB.†	·271
1,660	52,014	26·6	{ Clay Lane, No. 4 pig.	·311
1,320	51,593	28·6	{ Dowlais, No. 2 pig.‡	·203
1,147	51,597	23·7	{ Glengarnock, No. 2 pig.§	·170
1,251	46,547	21·0	Round Oak	·144
1,342	52,842	26·6	Butterley¶	·286

These results are perfectly in accordance with the isolated result obtained by Dr. Miller, and they indicate, I believe, an average amount of phosphorus, much larger than would have been generally considered to exist in malleable iron, presenting such a degree of tensile strength as that assigned to these bars, and so far as this character serves to indicate the quality of the

* Cleveland iron.

‡ Welsh iron.

|| Staffordshire iron.

† Northamptonshire iron.

§ Scotch iron.

¶ Derbyshire iron.

metal, it would appear to be very good. According to the determinations of tensile strength of bar-iron by Fairbairn,* Kirkaldy,† Napier,‡ and others, it amounts in the very best kinds of iron (Swedish and Lowmoor) to about 58,000 lbs. per square inch sectional area on the average, and ranges from 47,855 lbs. to 66,390 lbs., while the average permanent extension or drawing out of the bars, which furnishes an index of the ductility of the metal and its consequent power to resist the influence of a shock, amounts to about 24 per cent., and ranges from 20 to 28 per cent.

The number of analyses here given is, of course, much too small to admit of any general conclusion as to the amount of phosphorus which may be present in malleable iron without affecting its general quality and applicability for the various purposes to which it is applied; but in any case, as tensile strength is one of the most important qualities of iron, and as a high degree of that character appears to be compatible with the presence of a considerable amount of phosphorus in the metal, this fact has an interest in reference to the manufacture of iron from the very abundant iron ores of this country, which have been considered inferior, to a great extent by reason of the amount of phosphorus they contain. There are also other facts which tend to throw some doubt on the received opinion as to the influence of phosphorus. Thus, for instance, I can state as the result of my own observation, that throughout the whole iron districts of Belgium, the ores smelted contain, on the average, a very large amount of phosphorus; but, notwithstanding this fact, some very good malleable iron is produced there, although none of the Belgium pig-iron I have met with will answer for conversion into steel or malleable iron by the Bessemer method.

In addition to the bars of "steel iron" above mentioned, I also obtained portions of two bars of cast steel which were similarly tested by Mr. Kirkaldy, and on analysis, I ascertained the presence of phosphorus in them in the following amounts:—

* British Association Reports, 1856.

† Transactions of the Institution of Engineers in Scotland, 1858-9.

‡ Ibid.

No. of bar.	Tensile strength in pounds per square inch sectional area.	Permanent extension per cent.	Kind of pig-iron produced from.	Amount of phosphorus per cent.
1,077	80,916	3·3	{ Clay Lane, No. 4 pig, Stanton forge pig, BBB. Clay Lane, No. 4 pig, Stanton forge pig, BBB.	·240
1,082	106,602	13·7		·241

According to the observations of Fairbairn, Kirkaldy, and Napier, the average tensile strength of cast-steel bars and plates is about 100,000 lbs. per square inch of sectional area, and it ranges from 75,594 lbs. to 132,909 lbs., according as the metal is hard or soft. The corresponding permanent extension amounts on the average to 8·7 per cent., and ranges from 3·1 to 19·8 per cent. In regard to mechanical qualities therefore, the bars of cast steel, here referred to, come within the range of variation observed in high class steel. At the same time, the amount of phosphorus in this cast steel is very much more in excess of the reputed maximum amount that can exist in steel of such quality as is indicated by these mechanical tests, than it is in the case of the bars of "steel iron," and it is about tenfold as much as is stated to be present in the best kinds of steel. These results are therefore interesting, in so far as they show that the presence of such an amount of phosphorus in steel does not necessarily interfere with its possessing a high degree of tensile strength, which is one of the most important qualities for many of the purposes to which steel is now being applied.

It must be stated here that the samples of iron and steel analysed were produced by what is known as the Heaton method of converting pig-iron by means of alkaline nitrate.

I am unable at present to give any results which would serve to indicate the state in which the phosphorus may exist in the samples of iron and steel above referred to; but this seems to be a question deserving of inquiry, for as it is considered to be an established fact that steel or iron made by the Bessemer method cannot contain at the utmost more than $\frac{1}{1000}$ part of phosphorus, if its quality be good, the existence of such a much larger amount in the samples I have analysed would seem to indicate the possibility that if phosphorus be injurious in some cases,

still, under certain conditions, at least, it may be present without any such effect. It is my intention to carry out a complete examination of these samples with the object of elucidating, if possible, this question.

The analytical method by which the separation of phosphorus was effected in these analyses, was that by means of molybdic acid, and with the exception of the length of time required for the successful application of this method, it is one which I believe presents great advantages, especially for the determination of small amounts of phosphorus. The chief precautions I have found necessary to be observed, are to avoid the presence of any great excess of free acid in the solution to be tested; to have this solution as concentrated as possible before adding the molybdic solution, and then to give amply sufficient time for the perfect separation of the yellow precipitate. This separation is much facilitated by heating the liquid; but since arsenic acid reacts in the same manner as phosphoric acid, and gives a similar yellow precipitate when the liquid is heated to near the boiling point, it is desirable not to heat it much above 40° C. At least 24 hours should be allowed for the separation of the precipitate, and then it may be collected on a filter and washed with water containing about 1 per cent. nitric acid, and a mere trace of molybdate of ammonia, in which the yellow precipitate—containing only about 4 per cent. phosphoric acid—is so slightly soluble that the estimation of phosphorus is not sensibly affected.

For the determination of phosphorus or phosphoric acid, the weighing of the yellow precipitate, which may contain arsenic acid and silica, is less to be depended upon than converting it into phosphate of magnesia and ammonia by dissolving with ammonia and precipitating with a magnesia salt. The ammonia phosphate may either be weighed after drying at 100° C., and then tested for silica and arsenic, or ignited, and the pyrophosphate weighed as usual.

This method of estimating phosphorus in iron and iron ore is, I believe, much more to be depended on than any of the other methods hitherto adopted, with some of which there is much risk of an imperfect separation of the minute quantities of phosphoric acid from the disproportionately large quantity of iron.

VII.—On the Chemical Composition of Canaüba Wax.

By NEVIL STORY-MASKELYNE, M.A.

THE wax-like coating which protects the leaves and fruits of many plants has received little attention at the hands of chemists, mainly probably because its quantity is small, and the difficulties of collecting it in many cases almost insuperable.

In Canaüba wax, however, commerce supplies us with a material directly derived from a plant which furnishes such a wax in appreciable quantities. This vegetable wax is the product of a palm, the *Copernicia cerifera* of botanists, the Canaüba tree of the Brazilians. It grows to a height of 20 to 40 feet, and when young its trunk is covered with leaves, which, however, in the older plants are found only at its summit in a globular cluster. Its sap yields an amylaceous food, its wood is a valuable timber, while its younger leaves furnish in the glaucous coating that protects them, the wax-like body, the chemical nature of which the following investigation may contribute to elucidate. The leaves are shaken, after being detached from the tree, and the wax which they yield, to the amount of some 50 grains per leaf, is melted into a mass.

In this state it is a pale yellow body, with a faint tinge of green, considerably harder at ordinary temperatures than beeswax, and from the descriptions of the wax made from the noble palm, the *Ceroxylon Andicola* of the Cordilleras, it would seem to be also harder and less resinous than this latter body.

The specific gravity of Canaüba wax is 0.99907, and its melting point is about 84° C. On being incinerated it yields 0.14 per cent. of ash, for the most part consisting of silica and iron with some sodic chloride.

Many trials were made as to the best way of breaking this body up into its constituent compounds. The following methods were those ultimately adopted for the purpose.

A quantity of the crude substance was boiled with alcoholic solution of potash containing one-sixth of its weight of alkali, till the liquid became clear, when the spirit was distilled off. The residue, in which are contained the saponified products,

was poured into a solution of neutral plumbic acetate, a yellow colour immediately developing itself throughout the mass. The whole was then carefully dried, powdered, and extracted with ether. Wax alcohols dissolve in this liquid in large quantities, and mere successive crystallisation will give one of them, which seems to be melissin, in great purity. The insoluble lead salt can afterwards be decomposed by hydric chloride. In another experiment 12 oz. of the wax were saponified with an alcoholic solution of potash, as already mentioned; as soon as the liquid was clear, it was precipitated by cold water, the alcohol was then distilled off, and from the mixed soap and alcohols, which dissolve in the boiling water, the acids were set free by hydric chloride. The mingled mass of acids and alcohols thus formed was then dissolved in boiling alcohol, and the acids were saturated with ammonia; the ammonia soap, produced by this means, was next thrown down by baric chloride. The alcohol was now distilled off, and the precipitate, after having been thoroughly extracted with boiling water, was thrown on a filter. This precipitate was dried, powdered, and extracted several times with spirit. The residue was reserved for an examination of the acids contained in it.

The part dissolved by alcohol was extracted with ether. Repeated crystallisations from this liquid yield at length a substance melting at first at 87° , but ultimately rising to 88° . In this state the substance, when fused on a watch-glass, exhibits as it cools the concentric undulating rings characteristic of cooled wax alcohols. In appearance it is a very hard, semi-transparent, electric body, exhibiting when in mass but little crystalline structure, soluble in hot alcohol and in ether, though not in large amount in either of these liquids. From its alcoholic solution it separates, on cooling, as a gelatinous mass. From ether, on the other hand, it separates in small foliated crystals. Its analysis produced the following numbers:—

- I. 0.2858 grm. gave 0.8632 grm. carbonic acid and 0.365 grm. water.
- II. 0.2914 grm. gave 0.8824 grm. carbonic acid and 0.3738 grm. water.
- III. 0.2942 grm. gave 0.8898 grm. carbonic acid and 0.3768 grm. water.

These results correspond to the following percentages:—

	I.	Experiment. II.	III.	Theory. (C ₃₁ H ₆₄ O).
Carbon	82·37	82·6	82·46	82·30
Hydrogen ..	14·21	14·28	14·24	14·16
Oxygen	—	—	—	3·54
				<hr/> 100·00

The alcohol, from these numbers, was assumed to be melissin. In order to determine its constitution with greater exactitude, the homologous acid resulting from its oxidation was formed. This was effected in the usual manner: the tube containing an intimate mixture of the alcohol and potash-lime was kept by means of an air-bath at a nearly constant temperature of 270°, this point being never exceeded. Pure hydrogen was evolved for some hours and, when this gas ceased to be developed, the substance in the tube was removed and the acids were separated by boiling with hydric chloride.

The eliminated acids were dissolved in alcohol, and their solution was filtered whilst hot; when cold, the alcohol was removed by filtration. The precipitated acid was again dissolved in a very large amount of cold alcohol, and then boiled, after which this alcoholic solution was converted into an ammonia soap, and precipitated with baric chloride. This barium salt was filtered off from the boiling liquid, and repeatedly exhausted of any unoxidized wax alcohol it might contain, with boiling ether, the process being continued till the ether dissolved no further trace of substance. The barium was then removed by boiling the pure salt with hydric chloride. Dissolved in hot alcohol, and filtered from the remains of undecomposed barium salt, the melissic acid, after recrystallisation, presented, on being fused and broken, a fracture of highly crystalline aspect; and a fragment fused on a watch-glass gave, on cooling, the needle-like crystalline radiations which mark the cooling of the wax acids.

This substance was found to be in a high degree electrical; it melted at 91°, and was only with the greatest difficulty at all soluble in alcohol. Its analysis gave the following results:—

I. 0·2981 grm. gave 0·872 grm. carbonic acid and 0·36 grm. water.

II. 0·2972 grm. gave 0·8666 grm. carbonic acid and 0·3621 grm. water.

III. 0.2842 gram. gave 0.8286 gram. carbonic acid and 0.3462 gram. water.

These numbers corresponding to a percentage composition of—

	Experiment.			Theory.	
	I.	II.	III.	($C_{31}H_{62}O_2$).	($C_{30}H_{60}O_2$).
Carbon	79.78	79.51	79.49	79.83	79.65
Hydrogen..	13.42	13.53	13.55	13.30	13.27
Oxygen....	—	—	—	6.87	7.08
				<hr/> 100.00	<hr/> 100.00

The silver-salt of this acid was now prepared. An alcoholic solution of the acid, after saturation with ammonia in slight excess, was precipitated by an alcoholic solution of argentic nitrate, and the pure white precipitate filtered off and washed in the dark. Dried at 100° , it presented the appearance of a greyish-white powder, devoid of any waxy lustre, and very readily affected by the light. Its analysis gave the following results:—

I. 0.3692 gram. of the salt gave 0.8726 gram. of carbonic acid and 0.357 gram. of water.

II. 0.3276 gram. of the salt yielded 0.0632 gram. of silver.

III. 0.4192 gram. of the salt yielded 0.0816 gram. of silver.

These numbers correspond to the following percentage composition:—

	Experiment.			Theory.	
	I.	II.	III.	($C_{30}H_{50}AgO_2$)	($C_{31}H_{61}AgO_2$)
Carbon	64.46	—	—	64.4	64.92
Hydrogen..	10.75	—	—	10.55	10.65
Silver.....	—	19.29	19.45	19.32	18.85
Oxygen....	—	—	—	5.73	5.58
				<hr/> 100.00	<hr/> 100.00

In consequence of the large amount of alcohols yielded by the former process, I was convinced that these alcohols were present in the free state. To establish this, I endeavoured, in a fresh quantity, to separate them by direct crystallisation with alcohol, my preliminary experiments having proved the wax to be only partially soluble in that liquid. 400 grammes treated in this manner, after an enormous number and continuation of boilings, which at last barely removed a trace of substance, gave—

126 grammes of soluble ingredients, which melted at 81° ;

274 grammes of insoluble ingredients, which melted at 86° .

The *insoluble* portion, when saponified by potash, did not turn of so bright a yellow as the whole mass of wax does under the same treatment. This potash solution was then thrown down, as before, by a solution of lead, and the precipitated lead salt again dried, pulverised, and exhausted with alcohol. That part of the lead-salt insoluble in spirit corresponded to 85 grammes of acids, which were liberated from it by hydric chloride. From the portion dissolved in alcohol that solvent was distilled off, and the dried mass treated with ether. The boiling ether dissolved a number of wax alcohols, and left a residuary lead-salt which corresponded to 30 grammes of acids. The ethereal solution, on cooling, deposited mixtures of alcohols, from which, as before, successive crystallisations yielded large amounts of melissin.

The *soluble* portion of this fresh quantity, weighing 126 grammes, though repeatedly crystallised first from alcohol and afterwards from ether, yielded no products that after fusion on a watch-glass would give any crystalline substance as they cooled. This appeared to be due to a resinous body which, though very soluble in these liquids, adhered pertinaciously to the alcohols as they separated out on cooling. With a view to saponifying and precipitating this substance, a minute amount of potash was added to the alcoholic solution, which instantly turned very yellow and of a much brighter colour than was observed on subjecting the insoluble ingredients of the wax to like treatment; plumbic acetate threw down a precipitate comparatively trifling in quantity; and on boiling it in alcohol, it was noticed that the bodies which dissolved in this liquid no longer gave any yellow colour with potash. The resinous body thus eliminated in the form of a lead-salt, was too small in amount and too readily decomposed to invite further enquiry.

The mass of substance, now dissolved in alcohol, began, after a single crystallisation, to exhibit, on cooling from fusion on a watch-glass, the concentrically annular ridges peculiar to the class of wax alcohols. The ridges were far less coarse than in the case of cerotin, and a few crystallisations from alcohol and ether yielded an individual alcohol of great purity, which crystallised at 86° , and was, in fact, melissin.

The existence in the free state of a wax alcohol in Canaüba

wax, to the amount of about one-third of its mass, is a fact in vegetable physiology of no little interest.

The melissin thus obtained is invariably accompanied by another body in very small relative proportions to it, which is deposited in the flasks in fine crystals; it does not yield annular surfaces on fusion, but exhibits a crystalline structure of an entirely different kind.

It is a circumstance important to remark, that the melissin is present in much larger proportion to the mass of the other alcohols in the part soluble in spirit than it is in the portion insoluble in this liquid.

The whole of the residuary alcohols, both from the free alcohols in the soluble and from the alcohol bases set free from the insoluble part of the wax, were, after the separation of the first crystallisations of the melissin, mixed and treated together. Dissolved in boiling alcohol and filtered when cold, these mixed substances fused at a variable melting point of from 81° to 86° , and did not give a clear liquid at any temperature. By several recrystallisations more melissin was extracted and a body obtained which had a melting point of 87° , but which neither solidified in annular concretions nor presented the silky crystals characteristic of melissin. After these had been separated, the residues began to melt at 81° , and only became clear at temperatures over 90° . On treating them with benzol, there crystallised out a body having a melting-point of 88° , which by repeated recrystallisation from this liquid could be raised to 96° . After it had been crystallised from ether a few times, its melting-point was further raised to 105° , and at this stage it solidified with crystalline characters similar to those of cerotic acid, but did not saponify with an aqueous solution of potash. The residues of the solvents, from which this body melting at 105° had separated, yielded at once a substance that melted quite clearly at 84° , whence it may be concluded, that they contained no compound with a higher point of fusion. Substances crystallising between 80° and 84° are separated by the solvents from which this last body was obtained, but they are devoid of crystalline structure.

Owing to the small amount of these substances obtained from even so large an amount of wax as 400 grammes, a much larger quantity of the Canaüba wax was next worked upon, and the residues from the various stages of the treatment of these

400 grammes were mixed with the corresponding substances furnished by the new material. Two pounds of the wax were treated with a mixture of ordinary benzol and alcohol, a liquid which, not to mention its greater solvent power, has its extractive influence enhanced by its higher boiling point. A result of the latter fact is that the wax fuses and is thus more readily acted upon by the solvent. Each portion, as before, was saponified by an alcoholic solution of potash.

The *insoluble* part was precipitated by plumbic acetate. By operating on small quantities at a time, and allowing the flask to stand until the lead salt had fallen, the melissin could be poured off in a state of partial precipitation from the solvent before the latter had become cold; or it may be allowed to cool, when the lead salt will be found clotted into a lump at the bottom of the flask, thus enabling the overlying portion containing the wax alcohols to be mechanically separated with great facility. The lead salt, of course, is in this way only partially freed from melissin; it contains, however, none of the substance which melts at 105° . By again treating the mass thus separated from the lead salts, with the same solvents, the melissin may be obtained in considerable purity; it still, however, contains some lead salt.

The *soluble* part was saponified by potash in quantities of about 6 oz. at a time. By filtering the liquid before it had become quite cold, the solution of the soap was separated from a quantity of very nearly pure melissin, which a few crystallisations rendered colourless and absolutely pure. The soap in the filtrate was precipitated by plumbic acetate, and in this way a little more melissin was obtained. It must here be remarked that the mixture of benzol and alcohol used in treating this last quantity of the wax, dissolved some of the compounds of melissic and other alcoholic bases with wax acids, and that therefore the precipitate produced by plumbic acetate in the soluble part contained a small quantity of lead salts and of acids which properly belong to the insoluble portion.

After all the melissin had been crystallised out, as far as could be, from both the soluble and the insoluble parts, their residues were mixed and treated as one. Solution in alcohol and repeated crystallisation added to the amount of melissin obtained. The residuary matter contained in the filtrates from these last quantities no longer exhibited annular crystallisation on a watch-

glass; they consisted, in fact, of a mixture of the substance melting at 105° , with a number of lower wax alcohols, whose chemical isolation is a problem for which at present there is perhaps no known satisfactory solution. In order to separate the body which melts at 105° , these residues were then dissolved in a very large quantity of alcohol, sufficient, in short, to retain, even when cold, the more soluble of the wax alcohols. When cold this liquid was filtered, and upon the filter there was left a substance which, though it began to melt at 84° , did not become transparent till it reached a temperature of 92° . Crystallisation from pure benzol rapidly brought its melting point to 97° , and, this degree attained, no amount of re-crystallisation could raise it above this temperature. With ether, however, as already mentioned, several crystallisations gave a body having a melting point of 105° , which cannot by any means be further raised, and this was, in fact, the substance previously described. Although the filtrates from the preparation of this compound yield, by a repetition of the process of crystallisation from ether, a further amount of it, this body is present in but very small proportions in Canaüba wax. Enough, however, was at last obtained for examination and analysis. It crystallises from its ethereal solution in little bosses or lumps, radiating from a centre. Fused on glass it solidifies with crystalline characters, unlike, however, those of wax alcohols; and it is far less electric than melissin. Its analysis furnished the following results:—

I. 0.271 grm. of the substance gave 0.778 grm. of carbonic acid and 0.3352 grm. of water.

These numbers correspond to the subjoined percentages:—

	Experiment.	Theory.
	I.	($C_{39}H_{32}O_3$.)
Carbon	78.3	78.30
Hydrogen	13.73	13.71
Oxygen	—	7.99
		<hr/> 100.00

It is very difficult, however, to assign a formula to this anomalous substance, in the absence of more experiments as to its nature.

The filtrates from which the above body had crystallised,

yielded a series of substances melting respectively at 90° to 91° , 92° , and 95° ; these, however, were obviously mixtures.

The alcoholic bodies dissolved by the large amount of alcohol were next treated, with a view to a separation of the wax alcohols that they contain.

The benzol residues from which the substance melting at 105° had been procured were distilled to remove the benzol, and a considerable quantity of the spirit of the alcoholic solution of the lower wax alcohols was likewise driven off; these two residues were then mixed. On cooling, a large mass of mixed bodies was deposited, which were filtered off. This precipitate, of a dark colour, was then boiled with alcohol and animal charcoal, filtered once more whilst hot, and the spirit removed by distillation. By repeatedly crystallising this purified residue from ether, several bodies of the nature of wax alcohols were obtained; they were, however, necessarily in a state of only approximate isolation. Their melting points were more or less definite, being 72° , 73° , 75° , 78° , 80° 81° to 82° , 83° , and (a little melissin) 85° . There was, moreover, a small quantity of a substance melting at 84° , very similar to one melting at 78° ; this, however, was not melissin, and though cooling from fusion with highly crystalline characters, did not exhibit the annular kind of crystallisation. The alcohol melting at 78° appears to be that present in largest quantity, and is probably cerotin. The remainder of the above series were present in small, but pretty equal quantities. Sufficient of the alcohol which melts at 78° was obtained for the following analysis:—

I. 0.2722 grm. of the substance gave 0.809 grm. of carbonic acid and 0.3428 grm. of water.

These results correspond to the following percentage composition:—

	Experiment.	Theory.
	I.	($C_{23}H_{45}O$.)
Carbon	81.04	81.17
Hydrogen	13.99	14.12
Oxygen	—	4.71
		<hr/> 100.00

It may here be mentioned, that every attempt to obtain acids from these alcoholic bodies, by submitting them to the action of soda-lime, proved unsuccessful, from the fact of the lower acids

undergoing decomposition at the temperature necessary for the reaction with the higher ones.

In the endeavour to determine with greater exactness the nature of the alcohol, the iodide of its radical was formed. In the first instance this body was produced by the action of phosphorus and iodine, warmed gradually, and subsequently treated by boiling with water and a little sodic carbonate. The resulting substance was dissolved in benzol, and crystallised in large granular crystals. A similar preparation boiled with a strong solution of sodic carbonate gave a body with a melting point of 67° .

Subsequently the alcohol was treated by Von Fridau's method;* it was fused at a temperature of 120° to 135° C. in a sulphuric acid bath, a small quantity of phosphorus being dissolved in it, and iodine then added in excess. After being retained for some time at a temperature of 130° C., the mass was washed out with cold water, fused and shaken with water at 80° C. It was then dried and digested with ether, which left it with a melting point of 67° , having dissolved a body that separates from it with a fusing point of 70° to $70\cdot5$.

The comportment of the iodide with argentic oxide was then observed. A quantity heated with this oxide and a little water in a sulphuric acid bath to a temperature of 100° to 120° C. was converted into a pasty mass, which when dried and boiled with alcohol, was found to be soluble in this menstruum. As the solution cooled, an abundant deposit was formed of a body, the fusing point of which was found to be 67° . Hence it appears that this reagent does not act upon the iodide.

Analysis of the iodide produced by the above methods gave the following results:—

I. 0.249 grm. of iodide, prepared by means of phosphoric iodide, when burnt with plumbic chromate in a current of air, gave 0.2493 grm. water and 0.5946 of carbonic acid. A residue of unburnt carbon weighing 0.0015 grm. remained in the platinum boat.

II. 0.1009 grm. of the same preparation, when heated with lime and sodic carbonate, gave 0.0406 grm. of argentic iodide. The smallness of the quantity employed, magnifies the error of analysis.

III. 0.2085 grm. of iodide, prepared by Von Fridau's method,

* Liebig's Handwörterbuch, Bd. II, 924.

gave, when burnt, 0·2095 grm. of water, and 0·4902 grm. of carbonic acid. A residue of unburnt carbon weighing 0·0009 grm. remained in the platinum boat.

These numbers correspond with the following percentage composition :—

	Experiment.			Theory.	
	I.	II.	III.	(C ₃₀ H ₆₁ I.)	(C ₃₁ H ₆₃ I.)
Carbon	65·722	—	64·556	65·693	66·193
Hydrogen..	11·121	—	11·16	11·132	11·209
Iodine	—	21·744	—	23·175	22·598
				<hr/> 100·000	<hr/> 100·000

The behaviour of the iodide with ammonia and aniline was next examined. When dry ammonia was passed through the fused iodide at 150° to 160° C., it soon became turbid, and after the lapse of some time a white granular precipitate was formed in the fused mass. Heated with strong aqueous ammonia in sealed tubes, it invariably became opaque, and on breaking the points of these tubes under water they immediately filled. The compound resulting from each experiment, when boiled with water, evolved much ammonia, and had then a melting point of 68°·5 to 69° C., indicating a return to the state of simple iodide. This body, moreover, appeared to decompose spontaneously.

On boiling some of the iodide with aniline, and allowing the solution to cool, a precipitate formed. This was washed with cold ether, in which it is almost insoluble, and then boiled in this liquid, which dissolved it with great ease, and deposited it again in fine crystals. The product, when fused, evolved aniline, leaving a residue with a melting point of 68° to 69°.

The preparation of a corresponding chloride of the alcohol radical was next attempted. A quantity of melissin, after repeated treatment with phosphoric pentachloride, yielded a compound with a melting point of about 65°, which, however, sank to about 61° after warming the body with water. Boiling alcohol extracted from the above product a substance which fused at 64°·5, but after two crystallisations from ether was observed to melt at 65° to 65°·5. Two analyses of this substance gave the following results :—

I. 0·2201 grm. burnt in oxygen gave 0·2568 grm. of water, and 0·6035 grm. of carbonic acid.

II. 0.2154 grm. of a specimen, once more crystallised from ether, gave 0.246 grm. of water, and 0.5913 grm. of carbonic acid.

These numbers correspond with the following percentage composition:—

	Experiment.		Theory.	
	I.	II.	($C_{30}H_{61}Cl$.)	($C_{31}H_{63}Cl$.)
Carbon.....	74.784	74.865	78.861	79.065
Hydrogen ..	12.962	12.684	13.362	13.390
Chlorine	—	—	7.777	7.545
			<hr/>	<hr/>
			100.000	100.000

These closely agreeing numbers at first suggested that a chlorine replacement had taken place, or that a bi-chloride of the biatomic radical had been formed; an inspection of their composition, however, renders this scarcely probable.

	$C_{30}H_{60}Cl_2$.	$C_{31}H_{62}Cl_2$.
Carbon.....	73.32	73.66
Hydrogen ..	12.22	12.27
Chlorine	14.46	14.06
	<hr/>	<hr/>
	100.00	100.00

The body was therefore probably a mixture, a view which the change of melting point after treatment with water might be considered to confirm.

The acid produced by the action of sulphuric acid on melissin was also prepared, and its potash salt submitted to analysis. For this purpose the wax alcohol was heated with sulphuric acid in a water-bath, and continually pressed against the sides of the tube in which the operation was conducted, until it became completely dissolved, or rather perhaps suspended; by careful heating, merely a trace of discoloration is noticed. If, however, the temperature of the sulphuric acid be raised too high, and the wax be not stirred, the liquid soon becomes black, and much sulphurous acid is evolved. The wax, therefore, should never enter into more than incipient fusion. When taken up by the acid, it was dissolved in alcohol and saturated with alcoholic potash, which threw down a large white precipitate. Boiled repeatedly with water, this precipitate left a large flocculent residue, which when washed free from all sulphuric acid, was dried and examined. It was scarcely soluble in alcohol or ether,

and consecutive portions of these solvents removed about an equal amount, pointing to a slight solubility of the substance, and not an impurity of melissin. The purified body, thus obtained, fused at 96° . An analysis gave the following results:—

I. 0.165 grm., when burnt, gave 0.1681 grm. of water, and 0.3975 grm. of carbonic acid, and left in the platinum boat, a residue of sulphate of potash which amounted to 0.0249 grm.

These numbers correspond with the following percentage compositions:—

	Experiment.	Theory. ($C_{30}H_{61}KSO_4$)	($C_{31}H_{63}KSO_4$)
Carbon.	65.69	64.75	65.26
Hydrogen ..	11.27	10.97	11.05
Potassium ..	6.74	7.01	6.84
SO ₄	—	17.27	16.85
		<hr/> 100.00	<hr/> 100.00

The above analysis, like many of the earlier mentioned ones of the alcohol and its acid, points to the formula $C_{31}H_{63}KSO_4$, unless the trifling amount of blackening at its first formation may have caused an increase of carbon and hydrogen in the body.

The examination of the acids combined in the Canaüba wax, with the alcohol bases, remains to be completed.

The pertinacity with which a resinous body adheres to these acids, and refuses to be separated from them by any amount either of crystallisation from solvents or of partial precipitation by any one or by different salts, suggested the cautious use of a high temperature. By gradually raising the temperature to about 240° in an air-bath, the resinous substance was successfully grappled with, and acids obtained by crystallisation from alcohol and ether, which, on fusion and cooling, came to present the characteristic features of wax acids on a watch-glass. Acids with melting points from $90^{\circ}5$ and 80° — 78° to 40° , were thus obtained, but their further isolation and examination remains to be worked out.*

* The greater part of the investigation, of which this memoir is an account, was carried out by the author in the years 1855-7; other duties then interfered and have since prevented its completion. It is published now, because, no one having taken up the subject exhaustively in the interval, the author trusts the interest attached to the composition of Canaüba wax may induce some other chemist to complete its chemical history.

VIII.—*On the Chemistry of Sugar Refining.*

[A Discourse delivered before the Fellows of the Chemical Society, February 4, 1869.]

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THE science of chemistry embraces so wide a range of subjects, that there are few men who possess sufficient versatility of mind, or endurance of body, to undertake the study of every one of its numerous departments. Hence we find that, while all chemists regard original research as the highest aim of the profession, there are many who have rendered good service to the science, as literary chemists, teachers of chemistry, analytical chemists, assayers, metallurgists, and manufacturers. The Chemical Society has necessarily, and very properly, been chiefly occupied in the promotion of original work, but it has occasionally given some countenance to the scientific study of certain manufacturing operations, and I think I may say that the publication, in the *Journal*, of the papers or discourses on such subjects as the manufacture of glass by Mr. Chance, and the application of certain forms of furnace to the making of iron and steel by Mr. Siemens, has given great satisfaction to a large section of the Fellows of the Society, especially those who are non-resident, a large proportion of whom are interested in technical chemistry. In this country, unlike Germany and France, chemical technology receives no official acknowledgment from the State nor from the universities, and the thanks of those interested in that important branch of the science are due to this Society for the encouragement it offers to the prosecution of study and research in technical subjects. While therefore, I feel grateful to the Council of the Society for affording me the honour of delivering a discourse here this evening, I feel that I need offer no apology for bringing before them a subject of high utility, and one which possesses many points of interest to the scientific chemist.

The considerations which have induced me to bring before you the chemistry of sugar refining, are these:—First, the industry is one of very great importance; secondly, the trade has for some years been affected seriously by foreign competition; and, thirdly, the refineries in London, formerly the principal seat

of refining in this country, have for some time suffered from a very great depression, in some cases almost threatening annihilation.

As regards the extent of the industry in this country, a few statistics will suffice. According to the Board of Trade returns for 1868, the importation of sugar of all sorts amounted to 594,656 tons, or, in round numbers, 600,000 tons. This is charged at various rates of duty, but, if we take 9s. per cwt. as the average, the total revenue to the State from the import of sugar will amount to nearly $5\frac{1}{2}$ millions, and the total money value of the sugar, including duty, to about £21,000,000. I am not able to state what proportion of the quantity I have mentioned, enters into direct consumption, and how much is refined, but I think I am safe in saying, that at least 400,000 tons per annum are refined in this country.

The competition of foreign countries, particularly France, is entirely in loaf sugar, the quantity of which imported in 1868 was 34,039 tons, while the previous year it amounted to 42,047 tons. This is an alarming fact, and one that deserves the earnest attention both of our refiners and of our legislators. Either our refiners are far behind in the march of improvement in manufacturing processes, or the French refiners possess an unfair advantage in the shape of drawback on duty, which is equivalent to a premium offered by the French Government to the exporter of loaf sugar. That the latter is the fact I have attempted to show in a discourse recently published, and I will not occupy our time with a repetition of it. If our refiners are really backward in adopting means to keep up with the times, they deserve to succumb to the superior knowledge and skill of their continental neighbours; but if the other explanation of the enormous importation of loaf-sugar is the true one, then our Government ought to take steps to have the cause removed, and our own countrymen put on terms of equality with the French refiners. Besides the drawback on duty, to which I have referred, the French have a protective duty on foreign refined sugar, which makes it impossible for our refiners, under any circumstances, to export refined sugar to France.

Then, as to the depression of the trade in London, I think it depends upon a number of circumstances, but mainly upon the extraordinary development of the industry within the last few

years in Greenock and Glasgow. In 1857, the quantity of sugar refined in the Clyde was 38,336 tons, while in 1867, it rose to 178,013 tons, or considerably more than four times the amount. Last year the quantity refined was rather less, being only 171,643 tons, but even this is fully two-fifths of all the sugar refined in the United Kingdom. At present there are twelve refineries working in the Clyde, viz., ten in Greenock, and two in Glasgow, besides three standing idle or building, and besides these, there was refined last year about 11,000 tons by one house in Leith. Now, there are in London twenty refineries, in Liverpool eleven, in Bristol four or five, in Plymouth two, in Manchester two, in Newcastle-under-Lyme one, and in Dublin one; but of those in the metropolis, a considerable number are doing nothing. It appears to me that the London refiners generally have been somewhat tardy in adopting the most recent improvements introduced in the provincial refineries, and they have been unwilling to give up the making of loaf-sugar, which has not lately been profitable, for the reason I have named; and besides, they work under the disadvantages of dear labour and water not particularly well suited for the purpose; and, above all, they are prevented from reburning their own charcoal, and have to send it out to people who make a distinct trade of it. Thus, while in Greenock it costs 3*s.* 6*d.* to reburn a ton of charcoal, the same costs in London from 22*s.* 6*d.* to 25*s.*, thus inducing the refiner to use less charcoal than he would otherwise be likely to do. The description I shall give of the process of refining will refer to crushed or soft sugar, and chiefly to the Greenock system, the principal peculiarity of which is, that no syrup is produced; all the sugar leaves the refinery, as it came to it, in the solid form, and the loss, consisting of insoluble matter, compounds vegetable and mineral, abstracted by the charcoal, and loss in working, do not amount in all to more than 5 per cent. Whether this system is theoretically a correct one, I am not prepared to say, but at all events, it has been commercially successful; and the precision and rapidity with which the work is done appear to me to place sugar refining at the summit of perfection as a manufacturing process, and one which might, with great advantage, be imitated in many branches of technical chemistry.

Sugar Refining.

In refining raw sugar, it is very important to make a proper selection of the raw material. The qualities are very various, and each kind is adapted for a particular system of refining. In the Greenock system, for example, in which no syrup whatever is turned out, it is absolutely essential to use sugars containing only a moderate amount of uncrystallisable sugar, say not exceeding on the average 3 or 4 per cent.; but where a considerable quantity of syrup is produced, the quality of sugar is of less importance, and concrete and low sugar, such as syrup Mauritius, Jaggary, and Manilla may be used. Mixtures are often judicious, such as beet sugar with sorts which contain much fruit sugar, but in the Greenock system a large proportion of beet must be avoided, as the soluble salts accumulate in the lowest kind of the refined product, and communicate an objectionable taste, besides retarding crystallisation. In purchasing sugars for refining, several points demand attention. The absolute quantity of cane sugar is important, as determining mainly the proportion of refined capable of being produced; and the fruit sugar and salts, as preventing, to a large extent, the crystallisation of the cane sugar, demand attentive consideration. The extractive matter determines chiefly the amount of animal charcoal required, as well as the amount of deterioration of the charcoal. The insoluble matter, when excessive, is troublesome to wash, and some kinds of insoluble matter are difficult to filter, stopping up the pores of the cloth, which the finer particles pass through, and are afterwards deposited in the charcoal, to its great detriment. This is particularly the case with some kinds of East Indian sugar.

The analysis of sugar is very simple to those who have some practice in this kind of work, and most of our refiners pay great attention to this branch of their business. Many of them have qualified chemists in their refineries, while some employ a professional analyst. I have myself made about 400 analyses of raw sugar, chiefly for refiners in Greenock, and the following table contains a few results of analyses of some of the varieties of raw sugar used by refiners:—

	Cuba. Muscovado.	Grenada.	Trinidad.	Demerara.	St. Vincent.	Concrete.	Melado.	Molasses.	Pernambuco.
Cane sugar ..	92.35	92.31	90.41	90.80	89.00	84.20	67.00	47.0	88.31
Fruit sugar ..	3.38	4.06	3.84	4.11	5.85	8.45	11.36	20.4	4.82
Extractive, &c.	.66	.66	.95	.77	.76	1.70	1.93	2.7	.94
Soluble salts ..	.62	.37	.86	.92	.62	1.10	.76	2.6	.80
Insoluble15	.04	.22	.20	.05	..	.15	..	.73
Water	2.84	2.56	3.72	3.20	3.72	4.55	18.80	27.3	4.40
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.0	100.00
Colour, D. S...	13	13	10	10	10	12	8
Cane sugar } obtainable }	85.9	86.4	82.3	82.1	80	70.2	51.8	13.6	79.5

These analyses must not be considered as typical of the various kinds of sugar, for all of them vary exceedingly; but they give a fair idea of the description of sugars used in refineries where crushed sugar is made. Several of the lower sorts are unfit for refining on the Greenock system.

The French mode of determining the value of raw sugar is, upon the whole, a very fair one, and is based upon two assumptions, namely, 1st, that each percentage of fruit or uncrystallisable sugar prevents the crystallisation of an equal amount of cane sugar; and 2nd, that each part of soluble salt prevents the crystallisation of five times its weight of cane sugar. My own experiments bear out the general accuracy of these assumptions. To value a sugar, or find the amount of extractable cane sugar in it, we take the total amount of cane sugar, as determined by chemical analysis or the polariscope, and deduct from it the fruit sugar and five times the soluble salts, and the remainder is the quantity required. Thus, take as an example a sample of Paraiba sugar, containing 84.9 cane sugar, 6 of fruit sugar, and 1.2 of soluble salts, the obtainable cane sugar from this variety would be 72.9 per cent.

First Operation. Solution.

The first operation in sugar refining is dissolving, or what is technically called "blowing-up," from the circumstance that

Parado.	Bahia.	Syrup Mauritius.	Calcutta Date.	Jaggary.	Unclayed Manilla.	Amoy.	Formosa.	Maple.	Fr. Beet (fine).	Ger. Beet (low).
.90	86.80	86.00	87.06	86.73	79.00	74.50	76.53	72.60	94.30	87.80
.00	5.03	6.35	6.95	6.05	11.76	16.13	13.38	13.95	.25	.33
.23	1.72	1.62	.65	1.29	1.32	1.70	2.47	2.11	.27	.75
.20	1.21	1.44	.68	.88	1.95	1.61	1.86	1.35	1.30	5.92
.10	.92	.23	.56	2.01	.63	.54	.16	.03	..	.13
.52	4.32	4.36	4.10	3.04	5.34	5.52	5.60	9.96	3.88	5.07
.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
3	7	8	8	6	6	7	9	..	13	10
.9	75.8	72.5	76.7	76.3	57.5	50.4	53.8	51.9	87.5	57.9

open steam was formerly used in the process, producing a violent agitation and blowing noise. Although I do not purpose to detail the mechanical arrangements of the sugar refinery, yet I must mention briefly some particulars, in order that the chemistry of the subject may be understood. The different floors of a sugar house, generally six or seven, are arranged so that in the process the sugar passes down from one to the other. Acting upon this principle, the sugar is hoisted to the top story or garret, where it is removed from the hogsheads, boxes, baskets, or bags in which it is imported, and shovelled through holes in the floor into the blow-ups, which are situated on the floor below. These vessels are cast-iron pans, about 4 or 5 feet high, and from 6 to 10 feet in diameter. At some distance from the bottom, leaving room below for a series of steam pipes, is a false bottom perforated with holes, upon which the sugar rests until it is dissolved, and both above and below this shelf revolving arms are moved by machinery, so as to keep the liquor in constant motion. The operation is commenced by placing in the pan a sufficient quantity of water or thin liquor, turning on the steam to the heating-worm, and then filling in the sugar as quickly as it can be knocked out of the casks. If the blow-up is well constructed, the filling should be completed in half an hour, when the gravity of the liquor should be about 28° Baumé (or 1.225 sp. gr.) and the temperature as nearly as possible 180° F. The liquor consists of about two parts raw

sugar to one of water, and a pan of 10 feet diameter will dissolve at each filling about seven or eight tons of raw sugar. During the heating a scum rises to the surface, which is skimmed with nearly flat perforated ladles, but the amount of flocculent and insoluble matter so collected is very trifling. Such is the simple process as conducted in most of the Clyde refineries, but elsewhere the liquor undergoes in the blow-up various kinds of treatment, with the object either of removing a part of the colouring matter, of neutralising the trace of acidity in the sugar, or of facilitating the subsequent process of filtration, so as to produce a perfectly clear bright liquor. It is a very common practice to add a sufficient quantity of milk of lime or sucrate of calcium, in such quantity as to neutralize the acidity of the sugar, and although this is not done in some of the best conducted refineries, yet I consider it a useful addition, provided too much lime is not used, for if excess is employed it tends to deepen the colour of the liquor, and to give the charcoal additional work. Again, blood was formerly much used for clarifying, as it coagulates by heat, producing flocculæ, which enclose and carry down fine particles of mud or other insoluble matter. The coagulated albumin also abstracts a small proportion of the colouring matter, for which it has a strong attraction. Instead of blood, the solid albumin obtained by evaporating the white of eggs, or the serum of blood, at a low temperature, has been used, and has the advantage of not being quite so filthy as blood; but all these bodies, which make the syrups very impure, are now generally dispensed with. Various other substances have been used instead of blood, such as a mixture of sulphate of alumina and lime, which forms a gelatinous precipitate of alumina, but is objectionable on account of introducing calcic sulphate, soluble tricalcic phosphate, and soluble phosphate of alumina and lime. The greatest objection to these mixtures is the danger of the common workmen, who are necessarily entrusted with the application of them, using excess of one or other, and so making the liquor acid or alkaline, and thus doing more harm than good. Above all, it does not appear to be absolutely necessary to add anything to the liquor, and many of the first refiners use no chemical agent whatever. For the removal or partial removal of the colour of the sugar, the dust of animal charcoal is sometimes introduced, and if it is quite new, that is, not used in sugar refining previously, it has a good

effect. The charcoal can only be used once, however, as it gets mixed up with the insoluble matter of the sugar.

The next operation is a purely mechanical one, and consists in passing the solution of sugar through twilled cotton filter bags of about two feet diameter, crushed into coarse canvas sheaths of about 6 inches in diameter. These bags are 6 or 8 feet long, and are fastened, to the number of 200 or so, to the bottom of a shallow tank, into which the liquor is run from the blow-up pans, and they are surrounded by the sides of an iron box, so that the liquor is kept hot, and also that steam may be introduced to keep up the temperature.

Decolorising of the Syrup.

The next operation, after having obtained the saccharine solution clear and bright, is to remove the colouring matter, and this is effected by bringing it in contact with animal charcoal, otherwise called bone black. This variety of charcoal has been found by practical experience to be the most suitable for sugar refining. Many kinds have been tried, some of them, as decolorising agents, much more energetic than bone-black, but none of them have been found to possess that peculiar combination of qualities which is required—freedom from soluble salts and from considerable quantities of calcic sulphate or carbonate, sufficient density to sink readily in the heaviest sugar-liquor, and at the same time great porosity; together with such a degree of hardness that it will not suffer sensible deterioration by being shovelled about and reburned every fourth day for several years. These qualifications exist in no kind of charcoal in such a marked degree as in that from bones. An artificial mixture of clay and some form of carbon has indeed been made which is said to rival animal charcoal, but as I have heard nothing of it lately, I fear that it has not been found so advantageous as was expected. The only kind of charcoal I have found at all to approach that from bone, is the kind made from certain kinds of sea-weed, but even this variety is wanting in some of the characters necessary for refining sugar.

Other decolorizing agents than charcoal have also been proposed. Sulphurous acid has been tried repeatedly, and processes are published every two or three years in which its use is advocated, each writer apparently ignorant of the fact

that his results are already well known. At best it only removes about three-fourths of the colouring matter, and the liquor requires to be treated with charcoal just as much as if sulphurous acid had not been used. It is true that sulphurous acid does not alter cane sugar like most other acids, but it is very liable to change into sulphuric acid; and although this may be neutralized with lime, still the calcic sulphate is very injurious to the charcoal which must afterwards be used.

With regard to the bleaching action of ozone, I have made no experiments myself, but I understand that its application has not as yet been practically successful, and even if it were found economical in bleaching the colour, still it would not enable us to dispense altogether with charcoal, and I fear its oxidizing action would be likely to prove troublesome. Upon this point, however, I am not qualified to give an opinion, as I have not had an opportunity of seeing the process in operation.

The carbonatation process, as applied in the continental factories where sugar is made from the juice of the beet, and which is attended with excellent results, has not, so far as I know, been applied on the large scale to the process of refining raw cane-sugar, and I do not think its application would be advantageous. The sugar solution for this process requires to be rather dilute, and consequently would require to be boiled down before passing through the charcoal, for it would not be a substitute for charcoal, but only an adjunct to it. I have made careful trials of the process with dark sugar, and have found little or no benefit from it as regards colour, although it makes the liquor beautifully clear and bright. I think, however, that in certain cases it might be applied with good results, as for instance in purifying the washings of animal charcoal, which are very impure and very troublesome to deal with, and also to bag filter washings and any other impure products of the process of refining. To those who are not acquainted with the carbonatation process, I may describe it very briefly. The sugar, dissolved in a sufficient quantity of water, is mixed with milk of lime, the quantity depending upon the colour of the sugar to be treated, and, after being brought up to a moderate heat, carbonic gas is passed through the liquor until the lime is completely carbonated, after which it is boiled to decompose the calcic bicarbonate; and the precipitate then becomes grainy and settles readily. In the beet factories the process is repeated

with a smaller quantity of lime, after which the juice is boiled down to 20° or 25° B., and passed through charcoal.

Impure saccharine products, such as bag, filter and char washings, and low syrups much contaminated with salts, may also be purified by precipitating the sugar as a sucrate of calcium or barium, and afterwards separating the base by carbonic gas, or in the case of baryta, by sulphurous gas. I consider it an excellent arrangement to have connected with every large refinery, a smaller one immediately adjoining it, where all impure products are separately treated and worked up separately from the sugars made in the refinery proper.

As a preparation for the decolorizing process, it has been proposed to wash or digest the raw sugar with alcohol before dissolving in water, and this idea has been tried on the large scale in Belgium, but has been discontinued. Theoretically the treatment of raw sugar with alcohol appears to be highly advantageous. The quantity of cane sugar in a pure form obtainable from raw sugar is very much reduced by the presence of soluble salts and fruit-sugar, the former preventing the crystallisation of five times its weight, and the latter of an equal weight of cane sugar. By the use of alcohol, together with a minute quantity of hydrochloric or acetic acid to act upon the calcic salts present, the whole of the impurities, with the exception of some of the colouring matter, may be removed, and nearly pure cane sugar obtained. But in practice there are serious difficulties to be overcome. A very pure and nearly absolute alcohol must be used, and the expense of maintaining this would be considerable, and the inflammable nature of the spirit is a serious objection; but under any circumstances it would be quite out of the question unless the spirit were obtained free of duty. A moderate sized sugar-house would require something like 10,000 gallons of spirit to start with, and the duty on this alone would be about as many pounds sterling, and as this quantity would require to be re-distilled every day there would be a considerable and unavoidable loss. The process has long been used for testing raw sugar, and most successfully, but the possibility of its successful application on the large scale has yet to be demonstrated.

Filtration through Charcoal.

After this rather lengthy digression, we return to the process of sugar refining as it actually exists. After being made clear

and transparent by passing through the bag filters, the liquor is run into iron tanks or cisterns filled with animal charcoal, where it is allowed to settle for several hours, after which it is slowly drawn off below, while more of the dark coloured liquor is run on to the top, so as to keep the cistern full. As this goes on, the liquor, which comes away at first perfectly colourless, becomes after a time distinctly yellow, and the sugar solution is replaced by the syrup from a previous refine; and lastly, this is washed out with hot water until no appreciable trace of sugar can be found in the washings; then the charcoal is further washed with a copious volume of boiling water, next with some cold water, and afterwards drained, removed from the cisterns, and taken to the kilns to be reburned. Such, in few words, is the decolorizing process, which, however, I must now describe in greater detail.

The cisterns are of various forms and sizes; some are square and shallow, some of great depth, 40 to 60 feet, and so on; but the kind universally employed in the Clyde refineries are circular, and of no great depth, being generally about 9 feet diameter and 16 feet deep, and capable of containing from 20 to 25 tons of charcoal, according to its density. The cisterns are covered on the top, and are constructed to bear the pressure of a considerable column of water, or liquor, which may be applied when necessary, to cause a more rapid filtration. The quantity of charcoal to a given weight of sugar varies exceedingly. Where water is scarce or dear, coals dear, and, above all, where the charcoal has to be sent out of town to be reburned, the quantity of char is necessarily reduced as far as possible, but in other circumstances the proportion should not be less than 25 cwt. of char to a ton of sugar. The size or "grist" of the charcoal must depend to some extent on the shape and size of the cisterns; but in all cases where it is possible to use it, a small size, such as would pass through a sieve of 20 meshes to the inch, but would be retained by one of 30 meshes, should be chosen. Theoretically, the smaller the grist the better, the finest dust being the best of all, but practically the char must have a sufficient size to permit the liquor to pass through it in a reasonable time. Then as to the quality of the charcoal, it would occupy an entire lecture to go fully into that department. The whole subject is fully discussed in a lecture which I delivered last year in Glasgow,

and which will be found in the Proceedings of the Philosophical Society of Glasgow (vol. VI., part 4), also in abstract in the "Chemical News." On the present occasion I can only refer to some points connected with this most important subject. Animal charcoal, when new, consists of carbon, calcic phosphate and carbonate, and minute quantities of some other substances; the composition is a little variable, but the following results of analysis of three varieties will convey a good idea of its usual constituents, A being made from ordinary bones, collected in this country; B, from South American shank bones, and C, from what are called camp bones, which are frequently buried for some years before they are collected.

Dry.	A.	B.	C.
Carbon, nitrogenous ..	9.71	7.64	10.37
Calcic phosphate, &c. .	80.48	84.05	78.70
Calcic carbonate.	8.82	7.61	8.05
Calcic sulphate34	.20	.53
Alkaline salts30	.25	.58
Ferric oxide12	.15	.21
Silicious matters23	.10	1.56
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00
Cubic feet per ton (dry)	51	49	47

The above analyses represent the charcoal as being dry, in order that they may be compared with one another, but practically the article is always sold with about 10 per cent. of water.

The so-called carbon in animal charcoal is not by any means pure, for it contains a very notable amount of nitrogen, and a small proportion of hydrogen, the quantities of both of these elements depending upon the degree of heat to which the charcoal has been exposed in the process of manufacture. Generally the quantity of nitrogen is about one-tenth part of the total carbonaceous matter, but sometimes I have found it considerably more. The proportion of hydrogen in well-burnt animal charcoal is exceedingly minute, being in one particular case (new) only .034 per cent. Old charcoal which has been frequently used in refining, and reburned, contains less nitrogen, and the proportion appears continually to decrease. I have

found it as low as .3 per cent., and as the charcoal which gave this amount was not excessively old, I have no doubt it may be reduced even further. I believe that the nitrogen is an important and essential constituent of animal charcoal, and it is certain that no description of charcoal which does not contain an appreciable quantity of nitrogen is a good decolorizing agent. Wood charcoal, for instance, although eminently porous, and an excellent absorbent of gases, is a very poor decolorizing agent, and is practically useless. Red-hot animal charcoal quenched with water evolves ammonia, and I believe that the practice of cooling charcoal in this way pursued by some refiners is a highly injurious one.

New charcoal always contains traces of ammonia, but the amount is extremely minute, being in a particular case only .011 per cent. The effect of this minute quantity, and of traces of sulphide of ammonium is readily seen in the sugar run over new charcoal, which should never be used until after it has been well washed and reburned. New charcoal also contains invariably a minute quantity of sulphide of calcium, and gives off the odour of hydric sulphide when treated with an acid, and even when moistened with water. In a particular case a sample of new charcoal gave .08 per cent. of hydric sulphide when treated with an acid. Charcoal, both new and old, retains appreciable quantities of gases which escape when cisterns containing it are filled with liquor, and these gases frequently explode when a light is brought near the top of the cistern.

In a sugar-house the charcoal is usually burned every fourth or fifth day, and is thus reburned from seventy to ninety times in a year. Old charcoal has not the same chemical composition as new. The carbon almost invariably increases, and if the kilns are perfectly tight, ought to increase, so that the pores are gradually filled up with the deposit of carbon, arising from the carbonizing of the vegetable matter extracted from the raw sugar which it has been employed to purify. This deposit of carbon is a very great evil in sugar refining, and should be prevented, as far as possible, by washing the charcoal with boiling water before reburning. In some refineries the proportion of carbon does not increase, and in others it speedily diminishes, so that it sometimes does not exceed 2 or 3 per cent. When this decrease takes place, it arises either from the admis-

sion of air to the charcoal while hot, or from excessive burning, which causes a reaction to take place between the carbon and the elements of water, resulting in the formation of carbonic gas and marsh gas. But if the kilns and cooling boxes are tight, and the heat not excessive, the carbon will inevitably increase rapidly, unless we take the precaution of washing out of the charcoal, before reburning, nearly all the organic matters absorbed from the sugar liquor.

Extensive washing has also a most beneficial influence in removing mineral salts absorbed from the raw sugar. In all raw sugars a certain proportion of mineral salts is found, varying in ordinary cane sugars from $\frac{1}{2}$ to 1 per cent., in syrup sugars from 1 to 2 per cent., and in beet sugars, such as are used by the British refiners, from $1\frac{1}{2}$ to 7 per cent. The highly soluble salts, such as those of potassium, have no effect upon the charcoal, and only annoy the refiner by accumulating in the syrups; but calcic sulphate, a salt only slightly soluble in water, is readily absorbed by charcoal, and can only be removed by extensive washing. It is rather a singular fact, that so long as the sugar liquor is strong, the sulphate is absorbed and retained; but whenever the washing begins, it comes away in the washings, so that it is no uncommon thing in boiling down weak char washings, to obtain a plentiful crop, not of sugar, but of gypsum. When the water is hard, and contains much calcic sulphate, the proper washing of charcoal becomes almost, if not quite, an impossibility; and I have myself examined charcoal, which contained $2\frac{1}{2}$ per cent. of that compound. In beet factories where lime is freely used in clarifying the juice, the pores of the charcoal soon become choked with calcic carbonate, rendering it useless, unless the compound is removed by treatment with an acid.

But charcoal becomes old and useless from another cause; it gradually shrinks in volume, and the pores must become either lessened, or altogether obliterated. The space occupied by a ton of new charcoal, when dry, is usually about 50 cubic feet, but after being a few months in use it is reduced to 40; and so it goes on shrinking, until it reaches 28 cubic feet, which is the densest charcoal out of about 400 samples that I have tested. Now, this does not arise from an actual increase in the density of the charcoal. I have tried the specific gravity of old and new charcoal, and have found the difference very slight indeed. Thus,

new charcoal, occupying 50·6 cubic feet per ton, had a gravity of 2·822, while the old, occupying only 35 cubic feet, had a gravity of 2·857. The fact is, that the heat to which the char is subjected produces a semi-fusion of the calcic phosphate, which is its most abundant constituent, and causes a shrinking in the bulk of the particles. The following simple experiment serves to illustrate this point. A quantity of new charcoal, measuring 48 cubic feet per ton, was exposed, in a covered crucible, to a rather strong heat for an hour, after which it had contracted to 43·2 cubic feet; after two hours more to 40·8 cubic feet; after other four hours it measured 38, and with still four hours longer of a strong heat 35·5 cubic feet; thus losing in eleven hours as much of its porousness, as it would by being worked in a sugar house for two years. It is well known to chemists that calcic phosphate is fusible at a high heat, but the temperature of a charcoal kiln is sufficient to produce only agglutination. New charcoal burnt white has the appearance of bits of chalk, but old charcoal has the texture of porcelain or flint. The quantity of liquid capable of being retained by the two kinds is also remarkable. If a funnel is filled with good new charcoal, perfectly dry, and water poured on it as long as it is retained, it will be found to hold in its pores from 80 to 100 per cent., while old charcoal retains from 30 to 45 per cent. according to its quality. Again dry new charcoal does not become perceptibly wet, unless at least 20 per cent. of water is added to it, while old charcoal is made wet with 5 per cent.

All these considerations point to the necessity of renewing the charcoal very frequently, in order that it may act efficiently. It is not enough merely to replace the dust that is sifted out occasionally, and to make up by the addition of new char for the shrinkage in volume that is constantly taking place. If proper work is to be done, and the charcoal maintained in a state of real efficiency, a portion of the entire char (not the dust only) should be set aside from time to time and replaced by new material at the rate of 50 per cent. per annum, and the addition should be made constantly; one, two, or three bags of new charcoal in every cistern, according to its capacity.

As regards the proper quantity of charcoal to use, per ton of sugar, that depends a good deal upon the kind of sugar used, and upon the quality of the charcoal; but the smaller the quantity of charcoal the better, for the use of a large quantity

entails a loss of sugar and the production of an extra proportion of weak and impure washings. For a ton of sugar 25 cwt. of charcoal is amply sufficient if the quality is good, and if fine sugars are used, an equal weight is enough. It is a mistake to suppose that a large quantity of bad or exhausted charcoal will serve the same purpose as a moderate amount of good charcoal. Not only does it occupy more space, and so limit the production of refined sugar, but it does not, in any quantity, do the work so well, besides producing an overwhelming amount of "sweet water," or charcoal washings. I have found that it is impossible, on a practical scale, to wash out all the sugar from charcoal, so as to make the washings worth boiling down, and that for every 100 parts of charcoal there is a loss of $\cdot 75$ of sugar. If, therefore, an equal weight of charcoal is used, the loss of sugar will be $\cdot 75$ per cent., while if two tons of charcoal are used for each ton of sugar, the loss will be $1\frac{1}{2}$ per cent. from this source alone.

I have selected a few analyses of specimens of old or used charcoal which will convey an idea of the variety to be found in different sugar-houses throughout the country.

	D.	E.	F.	G.	H.	I.	K.	L.	M.
Carbon, nitrogenous	9 74	10 60	12 86	19 64	7 42	10 64	5 82	17 28	2 56
Calcic phosphate ..	82 80	83 20	81 80	73 20	87 08	80 56	77 26	79 56	90 73
Calcic carbonate ..	5 92	4 15	2 92	3 18	1 92	4 52	14 66	1 05	3 50
Calcic sulphate....	67	64	42	1 12	95	2 24	1 03	59	1 10
Ferric oxide	33	55	67	66	85	72	21	69	1 17
Silicious matters ..	54	86	1 33	2 20	1 78	1 32	1 02	83	94
	100 00	100 00	100 00	100 00	100 00	100 00	100 00	100 00	100 00

Cubic feet per ton..	44	39	36	32	29	35	40	34	35
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D is first-class charcoal; E is of excellent quality; F is of fair average quality; G is pretty old and very much glazed; H is very old and overburned; I has been used in a sugar-house where hard water is employed; K has been used in a continental beet factory; L has been soured in the process of washing; and M has been exposed to the air while cooling.

The power which charcoal is capable of exerting in removing colouring matter from solutions is truly astonishing. A very good lecture-room experiment consists in pouring into a funnel,

filled with good animal charcoal, an aqueous solution of cochineal, when it comes through perfectly colourless, and its presence in the charcoal in an unaltered form may be illustrated by boiling the charcoal with alcohol, when it gives up the colouring matter to that liquid. Port wine may be used for the same purpose and with a like result. Charcoal has also the power of absorbing vegetable albumin, gum, oxide of iron, calcic carbonate and hydrate, and calcic sulphate. In sugar we have vegetable albumin, extractive matters, and invariably some salt of calcium, and all these, as well as the colouring matter, are removed by the charcoal; and not only so, but their removal is important and essential, so that if we could practically bleach sugar by ozone, chlorine, sulphurous gas, or any other chemical agent, we should still require to use charcoal to purify the sugar.

The active ingredient in animal charcoal is unquestionably the nitrogenous carbon, for if the charcoal is burned perfectly white, not only on the outside of the grains, but to the very centre of each particle, it no longer retains the slightest trace of decolorizing power. But it is quite evident that the carbon owes its extraordinary powers to its extreme porosity, the carbon being infinitely comminuted and kept asunder by admixture with ten times its weight of calcic phosphate. The dark-brown solution of raw sugar comes away at first perfectly colourless; after a time the pores of the charcoal begin to get saturated, and the liquor gradually becomes yellow, and even brown if the process is continued long enough. The sugar refiner takes care to economize his charcoal by passing through it first a fine quality of raw sugar, afterwards an inferior sort, and lastly syrups from the drainage of previous refines.

The calcic carbonate in charcoal is very useful in neutralizing the minute quantity of acid present in almost all raw sugars, and also the acids always formed during the washing of the charcoal by a process of fermentation which it is very difficult to prevent. Charcoal deprived of all, or nearly all, its calcic carbonate is very objectionable, and is sure to give rise to sour liquors and the occurrence of iron in the syrups. When the water used for dissolving the sugar and for washing the charcoal is very soft, the calcic carbonate gradually decreases, until, in pretty old char, it is reduced to $1\frac{1}{2}$ per cent., and even in extreme cases, disappears entirely. On the other hand, when very hard water is used, the calcic carbonate either decreases

very slightly, or it increases, and sometimes to an alarming extent; and in beet factories on the continent, where lime is freely added to the juice, the evil is a very serious one. In this case it closes up the pores, and many expedients have been adopted for the purpose of getting rid of it. This is done either by washing with 1 or 2 per cent. of hydrochloric acid diluted with a sufficient quantity of water to saturate the char, or better, by Mr. Beanes' process, which consists in impregnating the burnt charcoal with perfectly dry hydrochloric gas until it is saturated, then exposing it to the air until the excess of the gas escapes, and, lastly, washing with water and burning. In beet factories, and, in some particular circumstances, in refineries also, when the liquors are slightly alkaline, the process is attended with the best results, but I have always objected to the use of acid in refineries using soft water, for there the calcic carbonate, instead of being in excess, is barely sufficient to neutralize the minute quantity of acid in the raw sugar. That animal charcoal treated with an acid, gives a whiter liquor than it would otherwise do is easily demonstrated; but, on the other hand, it appears from my own experiments and those of others, that it is impossible to get rid, by mere washing, of every trace of acid; and the consequence to be feared is, that the sugar in the liquor will be, to some extent, converted into fruit sugar during the process of boiling down, that the char washings will be very sour, and the syrups contaminated with iron. In other words, I believe that in a refinery working under ordinary circumstances, less syrup is produced than would obtain if the charcoal were treated with hydrochloric acid, while in the latter case the colour of the sugar produced would be superior. It may be interesting to mention that while dry hydrochloric gas, passed over dry calcic carbonate, does not give rise to any action whatever, the dry gas passed over absolutely dry charcoal containing calcic carbonate, determines the complete decomposition of the latter, especially if the charcoal is warm. Beanes' process, and others of a similar nature may be applied with advantage to new charcoal for the purpose of bringing it at once into efficient working condition. New charcoal contains traces of ammonia and sulphide of ammonium, and also some free lime, besides an excessive quantity of calcic carbonate; and although the ammonia is removed, and the free lime carbonated by the processes of washing and

re-burning, to which it ought always to be subjected before being employed in sugar refining; yet the excess of calcic carbonate makes the liquors very yellow, and it is usually five or six weeks before the charcoal is in first-rate condition. When, however, the new charcoal is added in small proportion to the old, there is no danger of any harm resulting, but, on the contrary, an immediate advantage is observed.

The oxidizing power of charcoal is well known to chemists, and although this property is useful in purifying water and in deodorising, yet in sugar refineries it is the cause of much mischief. When the char cisterns of a refinery are to be washed off, hot water is run on, while the heavier syrup descends and is drawn off below. But the two liquids commingle to some extent, and a weak solution of sugar is formed which is exceedingly liable to fermentation. The free oxygen in the washing water, under the influence of the charcoal, appears to act upon the vegetable albumin which the charcoal has extracted from the sugar, converting it into a ferment which quickly changes the sugar into lactic acid, and this acid dissolves from the charcoal lime and traces of iron. The consequence is that the char washings are sour and putrid, and highly charged with salts of calcium, besides which they frequently smell perceptibly of hydric sulphide. The ordinary way of getting rid of these washings is to use them for dissolving fresh sugar, but no greater mistake in sugar refining than this could be made.

As regards the temperature best adapted for the action of charcoal on sugar, experience has shown that the liquor in the blow-up pans should be run off at 180° F., the char cisterns should have a temperature of about 155° and never below 150° , and the water used for washing should be absolutely boiling. The quantity of water employed in the process of refining is, say for 100 tons of sugar, something like this:—for dissolving, 50 tons; for washing to produce sweet washings to be afterwards boiled down or used for dissolving, 40 tons; for washing the charcoal to purify it further, 125 tons—in all, 215 tons, or nearly 50,000 gallons. I consider this the minimum quantity; an additional amount of washing is invariably attended with increased excellence in the quality of sugar turned out.

Revivifying of the Charcoal.

The re-burning of charcoal, in order to restore to it the power of absorbing colouring matter and other impurities, is perhaps

the most important process in sugar refining. The object to be attained is to carbonize the organic matter extracted from the raw sugar, so far as it has not been removed by washing. The process should be economical as regards fuel; it should allow of the complete carbonization of the organic matters; it should permit of the ready escape of the gases and vapours produced; and it should expose the charcoal for only the smallest possible length of time to the heat required for carbonization, so as to avoid the contraction of the pores of the charcoal, besides other evils that result from overburning. There are two distinct kinds of reburners; those in which upright pipes are used, and those which consist of horizontal revolving cylinders.

The kiln in general use consists of a series of upright cast-iron pipes, arranged in six rows of about ten pipes each row, three rows being placed on each side of the furnace. The flame of the furnace plays directly upon the pipes, and the products of combustion are conducted away from the sides of the kiln. The wet char, as it comes from the cisterns, is placed upon the top of the kiln, and sinks gradually down as the burnt char in the pipes is allowed to fall into the cooling boxes below. These consist of sheet-iron vessels, the same length as the row of pipes to which they are attached, about six or eight feet deep, and an inch or three-quarters of an inch wide, and cooled simply by contact with the atmosphere. The cooled charcoal is drawn from the cooling boxes every twenty minutes, in such proportion that it is about six or eight hours in the pipes altogether. The time given should depend upon the heat of the kilns, and different quantities should be drawn from each row of pipes according to the amount of heat they receive from the fire. Thus, if there are three rows of pipes, the one nearest the fire should be emptied in about 5 hours, that in the middle in $7\frac{1}{2}$ hours, and the back row in 10 hours. These kilns, although tolerably economical as regards fuel, are open to many objections, not the least of which is that the wet charcoal above prevents the free escape of the gases and vapour evolved from the carbonizing and drying charcoal. Of the heat consumed in the kiln, four-fifths are absorbed in drying, and it is a great mistake not to dry the charcoal, wholly or partially, before putting it into the kilns. I cannot occupy more time with further details of the various mechanical arrangements which have been adopted by various sugar refiners, nor with the description of

the various forms of revolving cylinder-kilns, information about which will be found in my paper on charcoal, previously referred to.

When the charcoal is sufficiently cold it is again placed in the cisterns, and the whole process is repeated.

Evaporation of the Liquor.

The next process in sugar refining is the boiling down of the decolorized liquor, so as to recover the sugar in a crystalline form. This, as is well known, is effected by means of a vacuum pan, in which the vapour that is formed is condensed by jets of water, and the vacuum is maintained by means of an air-pump. A pan of good size is 10 or 12 feet in diameter, and may hold about 20 tons of sugar and syrup. The boiling down occupies usually about two or three hours; the extent of vacuum averages, in a well made pan, about 28 inches, and the temperature is usually 120° F. at the beginning of the boiling, and about 130° at the end of the process. The improvements introduced of late years into the vacuum pan consist in increasing the extent of heating surface, and the quantity of water injected into the condenser, and in enlarging the neck of the pan to 18 inches or even more, so as to permit of the free escape of the vapour into the condenser. The operation commences by running into the pan a quantity of liquor sufficient to cover the first coil of steam pipe or "worm," when the steam is turned on and the boiling commences. After a time more liquor is run in and so on, a little at a time, until the pan is full, the different tiers of worm being supplied with steam as soon as they are covered. At the very first the liquor is boiled strong enough to form a "grain," consisting of almost microscopic crystals of sugar, and these increase in size as the boiling proceeds, until at the finish they are as large as may be desired. It requires a considerable amount of training and skill to boil sugar so that the grain may be gradually built up. What is called false grain consists of a mass of minute crystals collected into grains, and although in some cases this kind of compound crystal results from the carelessness or want of skill of the boiler, in other instances it is made intentionally, so as to give the resulting sugar a whiter appearance, and to enable it to hold more syrup.

When very large and distinct crystals are desired, such as

are made in Bristol and Glasgow, a modified arrangement is adopted. The liquor is boiled more slowly and at a higher temperature, and when the pan is full the whole contents are not drawn off, but only a half, and this is repeated several times, the crystals becoming larger every time. The large crystals are much prized on account of their beauty and purity, but they have the disadvantage of being troublesome to dissolve, while the manufacture of them necessitates the exposure of the syrup with which they are mixed for a long time to a rather high temperature (about 160°) causing the conversion of a considerable portion of sugar into the uncrystallisable form, and also darkening the colour of the syrup. And here I would give a word of advice to refiners, who all insist that in order to obtain large crystals a high temperature must necessarily be employed. I believe this to be a mistake. If sugar requires a high temperature to form large crystals it must be different from all other crystalline bodies; and besides, sugar candy is formed at a low degree of heat, and consists of larger and more distinct crystals than ever were formed in a vacuum pan. Large crystals must be formed slowly, and the degree of heat is, I believe, a matter of indifference. Strange to say I have not succeeded in inducing any refiner to boil slowly and at a low temperature. They all say that it cannot be done, and so the matter rests. The mistake they make is, that they regulate the rapidity of boiling, not by the quantity of steam admitted to the worm, but by the quantity of injection water, so that, when the latter is diminished, the extent of vacuum is lessened, and the temperature necessarily rises, while the steam, not escaping readily, retards the process of evaporation. If, on the other hand, the maximum quantity of injection water were maintained, and the amount of steam diminished, the boiling would be as slow as might be desired, while the loss to the refiner by exposing the syrup to a high temperature would be avoided.

In boiling down the syrup obtained from the drainage of the first crop of crystals, less care is required, a small grain being preferred on account of carrying more syrup than a larger grain. In boiling the lowest grade of syrup it is customary to make what is technically called a "jelly," in other words, the formation of grain is entirely avoided, and the result is left for several days in tanks, in order that crystals may form: There are generally three qualities of crushed sugar made, viz., whites,

mediums, and yellows, the whites constituting nearly half of the entire produce; but the proportions of the different kinds vary to some extent with the kind of raw sugar employed. The total produce of 100 tons of raw sugar should not be less than 95 tons.

The separation of the crystals from the syrup with which they are mixed, is effected in an apparatus called a centrifugal machine, which is simply a perforated basket revolving at great speed, so that the periphery travels at something like 100 miles an hour. The drainage of the crystals occupies from three to twenty minutes, according to quality, and in the case of the finest and whitest variety, a dash of cold water is sometimes given in order to wash off the adhering syrup.

And now I must bring my lecture to a close, and have to thank you for the kind attention you have given to the subject. I feel that I owe some apology to the scientific chemists present, who must have listened, I fear, with impatience to details in which they can have felt little interest. I have endeavoured to avoid mechanical details as far as possible, while trying at the same time to exhibit a connected view of the whole process; and to the sugar refiners who have favoured me with their presence, I have to say that it is impossible in a single lecture to give anything like a complete description of all the improvements that have during the last few years been introduced, much less to describe the results of the investigations connected with this branch of industry with which I have been engaged. The field of inquiry is one that is sure to be fruitful of valuable results to any careful observer, and I trust that my few remarks, if not otherwise useful, may at least have the effect of attracting attention to a subject of great importance.

At the conclusion of the lecture, the President directed attention to the observations that had been made on the condensation of the charcoal in re-burning. He observed that charcoals not containing phosphate of lime, if they are subjected to a long-continued heat—which need not be very intense—gradually contract and become quite hard. He had found from his own experience that charcoal which has been produced in a very light and porous condition, gradually contracts on long exposure to heat, just as gold precipitated in the porous state by a ferrous salt becomes compact, and acquires a metallic appearance if heated far below its melting point.

The use of lime in sugar refining really appears to bring the sugar into an uncrystallisable state, and the power of crystallisation is not restored by addition of an acid, though it is recovered spontaneously after a certain time. The action both of acids and of lime and alkalies appears to destroy the crystallisability of the sugar, and therefore an excess of either should be avoided.

In connection with the decolorization of sugar, which appears still to be entirely dependent upon the absorbing power of animal charcoal, the President directed attention to the great absorbing power for colouring matters possessed by sulphide of lead, as observed some years ago by himself, in the case of a solution of cochineal, from which it entirely removes the colouring matter, although he by no means intended to recommend such a substance for use in sugar refining.

Dr. Hugo Müller said that the sulphide of lead cannot be used with advantage in liquids like sugar; indeed, Dr. Scheibler has recently found that it is dissolved and retained by several liquids of that kind, and cannot be separated from them afterwards.

Mr. Pearson stated, with reference to the quantities of sugar imported into this country, that Holland, as well as France, sends large quantities, and that unrefined as well as refined sugar is abundantly introduced. He mentioned the case of a sugar refiner in London, who about a year ago was refining at the rate of 400 tons per week of beet-root sugar imported from the Continent.

With regard to the washing out of the charcoal, Mr. Pearson observed, that in the north, where there is an abundant supply of pure water, this process may be carried to a very great extent; but in the south, where the waters, those of the metropolis, for example, generally contain a considerable quantity of calcareous salts, a limit is very soon attained, the charcoal after a certain time actually abstracting these earthy matters from the water, which consequently runs off purer than when it is put in.

The President enquired if any gentleman present could inform the meeting whether the colour-absorbing power of animal charcoal remains the same after the phosphate of lime contained in it has been removed by hydrochloric acid?

Dr. Hugo Müller said that he had found from his own experiments in filtration, that the pure charcoal, though actually stronger in its action than the ordinary bone-charcoal, is not so in proportion to the quantity; in fact, that the same quantity of charcoal, when the bone-phosphate is removed from it, is not so strong as if it contained the bone-phosphate.

Mr. Williams said that he could fully corroborate this statement from repeated experiments of his own; that though the pure charcoal will of course do more than the common charcoal, bulk for bulk, there is no comparison in the real percentage action of the carbon in each case.

Dr. Voelcker asked for information respecting experiments made by Mr. Beanes on the decolorizing effect of ozone upon sugar.

Mr. Beanes replied that the ozone process is not yet sufficiently advanced to enable him to speak positively respecting it; but that, so far as his present experience goes, ozonized air passed through a coloured syrup for three hours, exerts a decolorizing action as great as that obtained by leaving the sugar in contact with animal charcoal for twenty-four hours.

Professor Williamson observed that one of the most important points which have lately occupied the attention of sugar refiners, is the relation believed to hold good between the quantity of soluble salts in the unrefined sugar, and the quantity of crystallisable sugars retained by them in the mother liquid, and prevented from crystallising. It is customary now to estimate the quantity of such salts in the sugar, and to deduct a proportionate quantity of the sugar as being unavailable. From experiments made in his own laboratory by a gentleman occupied in the matter, it appeared that some salts possess the property of retaining sugar in solution as such, while others seem to possess the opposite property, actually accelerating the separation of the sugar.

Dr. Voelcker mentioned that beet-root sugar generally contains a considerable quantity of chloride of sodium, and yet no fruit-sugar is found in it, whence it seems to follow that chloride of sodium has not the power of changing the nature of the sugars. That it to a great extent prevents the crystallisation is, however, a well-known fact; indeed, sugar-refiners dread the presence of common salt in their sugars more than that of almost any other salt.

IX.—*On Catharism, or the influence of Chemically Clean Surfaces.*

By CHARLES TOMLINSON, F.R.S., F.C.S.

I PROPOSE to commence this lecture with an account of some experiments and remarks by three distinguished observers, whose names cannot fail to be received with respect in the Chemical Society. I refer to Oersted, Schönbein, and Liebig.

As long ago as the year 1805, Oersted published an account of an experiment* in which a solution of a carbonated alkali was filtered into a cylindrical glass, not too narrow, and upon this, with the beak of the funnel just touching the alkaline solution, was delivered, drop by drop, some dilute hydrochloric acid. At the moment when the acid drops touched the alkaline solution, there was a slight effervescence, but the gas was given off from the sides of the vessel, at the boundary line of the two liquids. Dilute sulphuric, nitric, or acetic acid might be used, and the alkaline solution might be that of carbonate of potash, of soda, or of ammonia, care, of course, being taken that the acid layer was of less density than the alkaline. Or a dense acid solution might form the bottom layer, and a less dense alkaline solution might be filtered upon this, until the volumes of the two liquids were about equal. The two strata remained quite distinct, as was seen by colouring the acid red, and the alkali green. The acid and the alkaline solutions could also be separated by means of a layer of water, in which case there was little or no effervescence on filtering the acid upon the alkali, or the alkali upon the acid. The liquids were to be filtered into the centre or along the axis of the jar. If the funnel were so inclined as to make the drops trickle down the side of the jar, there was a brisk effervescence.

But if the experiment were properly conducted, there was no escape of gas after the first slight effervescence. The glass might be left undisturbed during many hours without any appearance of gas, but the moment a solid was introduced, such as a platinum wire, a glass rod, a bit of shell lac, the finger, or any minute speck of solid matter, such a solid not only be-

* Gehlen's Journal, i, 276.

came instantly covered with gas, but discharged gas briskly from its surface. Oersted put his tongue into the jar, and, on examining it before a looking-glass, saw that it was covered with gas-bubbles. He also perceived the taste of champagne, and he argues that the tongue is efficient in separating gas from creamy wines. He also drew a much wider conclusion from his experiments, namely, that gas in solution is never given off except in contact with a solid.

In order to see whether any rise of temperature accompanied the escape of the gas, Oersted put a thermometer into the jar; the bulb and the whole of the immersed portion of the stem were instantly covered with gas. There was no rise in temperature, but thinking the thermometer would be more sensitive if covered with silver wire, he was surprised to find that the wire liberated gas even more abundantly than did the thermometer. There was, however, no rise in temperature.

Oersted confesses that he cannot account for the connection between a solid and the liberation of gas from solution, but he calls to mind many examples of such an action, as when water is put under the receiver of an air-pump, and the air exhausted, the sides of the vessel become covered with globules of air, and if a platinum wire be put into the water this, too, is similarly covered. So also, if a little dilute spirits of wine be poured into fuming nitric acid, and a glass rod be inserted, gas is given off from its surface, and still more abundantly from a platinum wire. Or, if a little dilute hydrochloric acid be gently delivered to a solution of potassium sulphide, there is scarcely any escape of gas or smell of hydro-sulphuric acid until a platinum wire is inserted, and then the gas is given off abundantly. He further remarks that every one knows the influence of a solid on the crystallisation of saline solutions, and also that water cooled below its freezing point, instantly becomes solid when touched. Blagden found that perfectly clean water was not readily frozen, but water containing particles that diminished its clearness, passed into the solid state with ease. Liquids that are set aside to ferment do not begin to give off gas until they become clouded with solid particles; if these be removed the fermentation ceases. In the effervescent drink made with carbonate of potash and citric acid, the two solutions mixed in a large glass, give off but little gas until stirred with a solid. If not stirred, the mixture, even after standing 24 hours, will

enter into brisk effervescence if poured upon the surface of a linen filter.

Thus far, Oersted. In 1837 Schönbein published a number of facts, pointing in the same direction as those contributed by Oersted.* He says that in the formation of gas or vapour in liquids, certain physical circumstances have an influence, and may even produce decomposition; as, for example, when a solid is put into a solution of nitrous acid, or into nitric acid containing some of the lower oxides of nitrogen. If such acid be covered with a layer of water, and a platinum wire be passed down to the boundary of the two liquids, a lively effervescence takes place, nitric oxide being liberated. Gas is also given off abundantly when copper, brass, iron, or silver wire is put into so dilute a solution as one part of nitrous acid to ten parts of water. The escape of gas is far too copious to be accounted for by chemical action; indeed, there is no such action, for there is not only no rise in temperature during the strongest effervescence, but actually a slight fall. Moreover a bit of pine wood liberates gas with nearly as much energy as a brass wire, but if the wood be deprived of air by long boiling it becomes inactive. It is, he says, of importance to the interests both of physics and of chemistry to be able to explain these phenomena. It seems likely that the solids act by carrying down air, into which the gas expands, and that when deprived of air they are inoperative.

In 1839 Liebig, while giving the details of an analysis of a mineral water,† noticed some phenomena connected with the liberation of gas from solution by the contact of solids, as when sugar is thrown into a mineral water containing much gas, it produces a lively effervescence; or, if a stoneware bottle, filled with such water, be well shaken, so much gas may be set free as to drive out the cork; so also if the mouth of a glass containing an effervescent wine be suddenly struck with the palm of the hand, a foam appears on the surface. In all these cases air plays an important part. There is air in the pores of the sugar, there is air in the stoneware jar, which by shaking mingles with the water, and air also is driven into the wine by the sudden blow of the hand. Now, taking into account the relative solubilities of air and of carbonic acid gas, it will

* Poggendorff's *Annalen*, xl, 382.

† *Ann. Ch. Pharm.* xxx, 13.

follow that for every cubic inch of air driven into the water, twenty cubic inches of carbonic acid will be set free.

Such are the facts and remarks contributed by three first rate observers in science.

Similar facts may be multiplied, not only as it relates to the liberation of gases from solution, but also of vapour from boiling liquids, and the crystallisation of saline solutions. Thus in the Scotch distilleries, in converting the "wash" into "low wines," it is customary to throw a lump of soap into the still every time it is charged. The effect is to cause the steam to rise quietly. The sugar-boilers also are accustomed to throw a lump of butter or of paraffin into the vacuum pan, for the purpose of preventing that irregular kind of boiling which displays itself in furious bursts, separated by almost passive intervals. It is also a usual practice in the laboratory during distillations, to introduce into the retort, solid matter, such as sharp or angular pieces of metal, glass, &c., the points being supposed to favour the generation of steam, and prevent *soubresauts* or jumping ebullition. So also, in crystallisation on a large scale, strings stretched across the vessel, or a cinder thrown in, favour the formation of crystals.

But whether gas, or vapour, or salt escape from solution, the influence of some mysterious function in the air is asserted by most writers. Thus Le Grand,* who paid great attention to the phenomena of boiling, says, as De Luc had done half a century before, that as soon as the liquid, water for instance, has discharged all its air, the boiling becomes difficult and irregular; indeed, De Luc denies that water can boil at all if completely purged of air. Le Grand, referring to the use of platinum for preventing bumping, on account of its unalterable character, says it is a mistake to employ that metal, for as soon as the air introduced by it is expelled by the heat the bumping is renewed. He recommends zinc or iron—metals that decompose water with the greatest facility.—and of the two zinc is to be preferred.

Writers also frequently refer to changes in the molecular condition of the vessels containing gaseous or saline solutions, or boiling liquids, to account for unexplained phenomena. The idea originated with Gay-Lussac, in his paper published in

* Ann. Chim. Phys., lix, 426.

1817,* on the shifting of the boiling point of liquids under a constant pressure in vessels of different materials. He imagines the boiling point to vary with the nature of the vessel, and in the same vessel, with the condition of its surface, its degree of polish, and also its conducting power for heat. The cohesion or viscosity of the liquid, and its adhesion to the sides of the vessel, must also exert an influence on the boiling point. So also in 1819† he explained the state of supersaturation of sodic sulphate on similar grounds, such as the nature of the containing vessel, its state of polish, its conducting power, the influence of electricity, and a particular disposition of the saline molecules, by virtue of which they resist, more or less, their change of state.

Gay Lussac exerted so powerful an influence on the scientific mind of France, that any suggestion thrown out by him took deeper root than he perhaps intended. Moreover, he was a man of lively imagination and inventive power, and would readily throw off half a dozen suggestions to account for phenomena that were not clear to him, without always stopping to test these suggestions in the crucible of experiment. But later observers, with less invention, regard these suggestions thrown off so carelessly by Gay-Lussac as pearls of great price, and estimate and cherish them as the talismans which are to explain some of nature's mysteries.

One of the greatest authorities on the subject of supersaturated saline solutions is the French chemist Löwel, who devoted eight or nine years of conscientious labour to the study of this subject, the result of which is given in six elaborate memoirs,‡ in all of which he relies upon a theory of molecular changes to account, not only for the leading phenomena of supersaturation, but also to explain many anomalous cases, and this theory was applied as well to the solutions themselves as to the sides of the vessels containing them. Thus, to select two or three passage out of many, he says—

“I think that at these low temperatures the inner surfaces of the tubes and flasks usually reassume their *active* or *dynamic* property of determining crystallisation, which heat had deprived them of.”

Again, he says, with reference to the formation of the modified salt:—

* Ann. Chim. Phys., vii, 307.

† Ibid., xi, 296.

‡ Ibid., 1850 to 1857.

"There is every reason to believe that the walls of the vessel do not perform a merely passive part."

And again—

"Such solutions remain supersaturated until, in consequence of lapse of time, and above all of low temperature, the inner surface of the phials have recovered that particular property of determining crystallisation, of which heat had deprived them, the cause of which is unknown to us."

Löwel also regards the functions of nuclei in determining crystallisation "as the effect of one of those mysterious contact actions, known as *catalytic*, of which science has not yet been able to give a satisfactory explanation."

I cannot help thinking that of late years the terms "molecular change," "molecular force," "molecularity," &c., have been applied to phenomena in physico-chemistry without always sufficient discrimination. As used with respect to a large class of phenomena, such terms do not advance our knowledge at all, and every time we displace the word "molecular" by a simple, common sense explanation of the phenomena in hand, we perform, in my opinion, a real service to science.

Of the varied examples which I have thus selected from the labours of others, Oersted gives no explanation at all; Schönbein accounts for his facts by reference to the action of the air, which, however, he thinks insufficient; Liebig endeavours to explain the phenomena brought forward by him, by means of the displacing power of common air over carbonic acid, but for this he gives no experimental proof; Gay-Lussac offers a number of suggestions by way of explanation of his facts, and from him Löwel and others have derived the idea of "molecular change," and from Berzelius that of "catalysis."

In appearing before you to-night with a new scientific term, I may seem to be guilty myself of the fault which I condemn in others. But I venture to submit that if the term "molecular change" is, according to my view, a vague one in physico-chemistry, the term "catharized condition" has at least the merit of clearness. The Greek word *καθαρος* signifies "pure" or "clean," but the cleanliness of matter implied by "catharized" is very different from what is usually understood in the ordinary application of the word "clean." Oersted found his finger act as a nucleus in liberating gas from solution, but no amount of cleaning would have made it otherwise than unclean

in the sense now intended. But if Oersted had cleaned his glass rod or platinum wire in a caustic alkaline solution, or in sulphuric or nitric acid, and rinsed it well in clean water, he would have catharized it, or made it chemically clean, and it would then have no longer liberated gas from his solutions, or salt from supersaturated or other solutions, or vapour from a liquid at or near the boiling point.

When bodies act as nuclei in separating gas, or salt, or vapour from solution, it is because the gas, or the salt, or the vapour has a stronger adhesion to, or attraction for, the surface of the nucleus, than the liquid portion of the solution has for such surface. If the nucleus be chemically clean, there is no appreciable difference between the adhesion of the gas and such surface, and the liquid that holds the gas in solution. Hence there will be no separation of gas, because the solution adheres perfectly and as a whole to a catharized surface.

Bodies that are exposed to the air, and to the products of respiration and of ordinary combustion, that are handled, or wiped with a cloth, contract more or less of a greasy film, which lessens the attraction between the liquid portion of a solution and such surface, while the attraction between the gas, &c., of such solution remains the same as before. Hence there is a separation of gas, &c., from solution, since gas, or salt, or vapour will adhere perfectly to a greasy surface, and the attraction between such a surface and a gas is so strong as, in some cases, to produce chemical decomposition, as when chloride of nitrogen is touched with an oily or greasy surface.

The dust of a room, which is constantly floating in the air, is more or less contaminated with greasy or organic matter, and acts as a nucleus. If such dust be collected on a filter, and washed with a solution of caustic potash, rinsed with water and dried out of contact with air, it ceases to act as a nucleus.

A nucleus, then, may be defined as a body that has a stronger adhesion for the gas, or the salt, or the vapour of a solution, than for the liquid which holds it in solution.

I believe this new principle of catharism is sufficient to generalize and account for, in a scientific manner, the numerous facts already introduced to your notice. When Liebig shook a bottle half full of a carbonated mineral water, the gas was liberated by coming into contact with the unclean sides of the vessel. When he struck his hand on a glass containing sparkling

Moselle or other gaseous wine, he not only precipitated some of the unclean dust of the air upon it, but he also shook the wine against the unclean sides of the glass. If a bottle of soda water be gently poured into a catharized glass, not a single bubble will become attached to the sides. If water in a similarly clean glass, containing a clean glass rod, or wire, be put under the receiver of an air-pump, and the air be exhausted, not a single bubble of air will attach itself to the sides of the vessel, or to the glass rod, or to the wire. When Schönbein found a bit of pine wood, by long boiling, inactive in liberating gas from solution, it was not that the boiling had driven the air out of the wood, but that the boiling had catharized the wood. There is not a greater mistake than to suppose the air to have an influence in setting gas, or salt, or vapour free from solution. When air appears to act it is merely as a carrier of some unclean mote or speck of dust that is floating in it. And this explains the fact noticed by Löwel and others, that supersaturated saline solutions can be kept longest without crystallising in narrow-necked vessels, the time being long in proportion to the narrowness, so that if the mouth of a vessel be contracted to a capillary bore, the solution can be kept as in a close vessel. I have found that highly charged supersaturated saline solutions in wide-mouthed flasks can be opened in a garden or a field in the country where the air is free from the dust and motes of a room, and be kept open for a long time without crystallising, and when crystallisation does take place, a nucleus is to be found in the shape of a small fly or other unclean object.

By attending to this principle of catharism, we may be able to account for, and to eliminate those anomalous cases of crystallisation which have given rise to such terms as "the mysterious action of the air," "the altered molecular condition of the sides of the vessel," "the molecular change which takes place in the solution," &c. Previous observers are, I believe, agreed as to the sensitiveness to cold of supersaturated saline solutions. According to them, there is no separation of salt from solution during the summer months, but the first touch of autumn's or of winter's cold immediately produces a deposit of salt. Hence, according to Löwel, whose view is generally adopted, a supersaturated solution of the ordinary ten-atom sodic sulphate undergoes no change so long as the temperature is about 60° F.; but below this it undergoes a molecular change, and assumes the

constitution of the more soluble seven-atom hydrate. Hence he ingeniously argues that supersaturation is a phenomenon in appearance only and not in fact, for the solution is but an ordinary saturated, not supersaturated, solution of the more soluble seven-atom hydrate. Why, I have had highly charged supersaturated solutions of sodic sulphate (five salt to one water) in catharized tubes in freezing mixtures at 10° F. for hours together, without any separation of the salt! And this observation applies not to sodic sulphate merely, but to a number of other salts that form supersaturated solutions. Highly saturated boiling solutions of sodic acetate, of sodio-potassic tartrate, of sodic arseniate, of potash alum, &c., may be cooled down to near the zero of Fahrenheit without showing any sign of crystallisation. A salt of greater solubility is not formed, and the state of supersaturation, so far from being one in appearance only, and not of fact, is one both of fact and appearance.

Take the case of potash alum. This is one of those salts which, according to some observers, throws down crystals in abundance when a hot saturated solution is left to cool in a close vessel. This is a true observation if the experiment be conducted in a vessel that is not chemically clean, but if a strong solution of alum ($3\frac{1}{2}$ salt to 1 water) be boiled in a chemically clean flask, and then filtered into a similar flask, boiled again, and a plug of cotton wool be fitted into the neck, not only will such a solution cool down to the temperature of the air without any separation of the salt, but the flask may be kept in a freezing mixture of ice and water for hours, without any sign of crystallisation, although the solution contains upwards of sixty times more salt than the water can take up at the reduced temperature.

It was not known that the inner surface of a chemically unclean flask acts as a nucleus on the solution as it cools down. Löwel often noticed the embarrassing fact that at low temperatures the sides of his flasks appeared to regain the active condition that heat had deprived them of, and seeing that the glass rod and other solid nuclei, which had been rendered inactive by means of flame, or by long immersion in water, and cooling or drying out of free contact with air, became active by exposure to the air, he naturally attached some mysterious property to the air, yet to be discovered. All these anomalies disappear by making use of chemically clean flasks with carefully filtered

solutions. The state of supersaturation then resolves itself, in the majority of cases, not into the formation of a more soluble salt, but into a case of *no nucleus*, in fact, into the absence of any predisposing cause that influences crystallisation.

We must even modify our ideas as to the influence of low temperature in inducing crystallisation. I think it a remarkable fact that alum, for example, of which 3.9 parts dissolve in 100 of water at 32° F., and 357.58 parts in the same quantity of water at 212°, should allow a solution containing upwards of 60 parts more salt than it can dissolve at 32° to be cooled down to that point, and even below it, without any separation of the salt. And this is not a state of unstable equilibrium which it is difficult to maintain, for such a solution in a bottle half full of air can be violently shaken, or kept for a length of time without change, or put into freezing mixtures, or be exposed to various vicissitudes of temperature. It had not been hitherto supposed that highly saturated solutions could thus be made independent of low temperature. Since Löwel's time, the course of inquiry has been chiefly directed to ascertaining the real function of nuclei in inducing crystallisation. Solid bodies have been examined by hundreds in the hope that in this multiplicity of examples a few might be got to speak the truth. My own labours in this direction, conducted during a long period, with a great respect for the authority of Löwel and others, led to very contradictory results. By slow degrees it began to dawn upon me that in the simplicity of nature's dealings a slight difference in the force of adhesion between the nucleus, the solvent, and the thing dissolved, was sufficient to explain the matter.

A great many salts form supersaturated solutions. Only a few produce the modified salt of a lower degree of hydration, and of greater solubility than the normal salt. My explanation of the formation of the modified salt, when it does occur, has already been published, in full, elsewhere,* but I shall have occasion to describe it, in brief, presently. In the mean time I may be allowed to remark that if Löwel's molecular theory were true, it ought to apply to all salts that form supersaturated solutions. Indeed, it is so applied by Löwel's followers, and they explain supersaturation by supposing the molecular character of every solution to change on a certain depression of

* Phil. Trans. for 1868, page 666.

temperature, so as to assume the condition of greater solubility of the more modified salt. Löwel, in the course of his long inquiry, extending as it did over eight or nine years, never succeeded in showing that more than about three salts formed the more soluble modified salt, and his followers have done nothing to add to the number. Anomalous cases occur which cannot be explained except in a way which seems to me to be fatal to the theory. For example, to notice only one such case. Löwel poured a strong boiling solution of sodic sulphate into two bottles of the same size, which were then tightly corked and set aside to cool under apparently the same conditions. The solution in one of the phials deposited the modified seven-atom salt, while the solution in the other became solid throughout as the normal ten-atom hydrate. Löwel supposes that in one case the solution did undergo the molecular change which led to the formation of the seven-atom hydrate, while in the other case, from some cause or other, the molecular change did not take place. My explanation is this:—The one bottle was cleaner than the other, or was made so by the hot solution. As the solution cooled down it deposited the excess of anhydrous salt which it could no longer hold. The heat thus liberated, and also a rise in atmospheric temperature after sunrise, caused the anhydrous salt to re-enter into solution, and to form a dense lower stratum, from which the seven-atom hydrate in small quantity crystallised out, there not being sufficient water in this dense stratum to form the ten-atom hydrate. In the other case the solution, during the cooling, met with a nucleus high up in the bottle, to which the salt could attach itself, and the action, once begun in the presence of a nucleus, was propagated rapidly throughout, the needles having sufficient, or carrying down sufficient water to form in every part of the solution the ordinary ten-atom salt. Cases of this sort have repeatedly happened to me in the course of my investigations. If we open a flask containing a supersaturated solution, crystallisation sets in at the surface, consequent on the entrance of some speck of dust from the air, and the needles proceed from the surface to the bottom, solidifying the whole contents of the flask; whereas the modified salt, when it forms at all, invariably does so in small quantity at the bottom of the flask, while the superposed mother-liquor is still a supersaturated solution. If the flask be now opened, the normal salt forms on the surface, crystallisation

proceeds rapidly downwards, and the needles seem to interpenetrate the transparent modified salt, giving it, in the case of sodic sulphate, three additional equivalents of water, and rendering it opaque in the process.

The action of nuclei explained, according to my view, with reference to gaseous and saline solutions, applies equally well to the liberation of vapour from a liquid at or near the boiling point. Such a liquid may be regarded as a supersaturated solution of its own vapour. If the vessel in which the liquid is boiled be chemically clean, or becomes so by the action of the liquid, the vaporous solution adheres perfectly and completely to the sides, but as the heat is continually acting, the liquid becomes more and more saturated with the vapour, until, not being able to dissolve any more, it relieves itself by a sudden burst as from a safety valve. This sudden burst of vapour occasions the jumping or rebound of the vessel by a mechanical reaction. The burst of vapour follows the direction of the line of least resistance, or upwards, along the axis of the vessel; this produces an equal reaction in a downward direction, which tends to force the vessel further into the ring of the retort stand, and it is the rebound from this that constitutes the *soubresaut* or the phenomena of *bumping* or *jumping* ebullition. This explanation, which I venture to give, may be tested by suspending a flask or a tube, by means of a spiral spring or a thread of elastic, against a board, with a line drawn horizontally from the mouth. If the vessel be chemically clean, or contain one of those solutions, which, according to Le Grand, favour the production of sobresauts, it will be found, on the application of a spirit-lamp, that every burst of vapour is accompanied by a downward kick of the vessel. If with the view of preventing soubresauts, we throw into the vessel a solid of any kind that has been handled or exposed to the air, the violent action is got rid of, because the vapour attaches itself to such solid with greater force than the liquid does, so that, under the action of the heat, there is a constant liberation of vapour from the surface of the solid. But should the liquid be of such a nature as to bring the solid into a catharized condition, the bumpings return with even more violence than before, because we have now increased the adhesion surfaces, instead of the vapour-giving surfaces. If, instead of an unclean body, we introduce a catharized body into a vessel in which a liquid is boiling with

little or no bumping, we may at once bring about such violent bumping as to endanger the safety of the vessel. A little sand, steeped in strong sulphuric acid, and well rinsed in water or in a weak alkali, is sufficient for the purpose in a flask in which distilled water is boiling. Even the iron on the zinc, so much insisted on by Le Grand as favouring tranquil boiling, produce *soubresauts* if made chemically clean. Zinc, however, often contains minute specks of porous matter which act in another way, as will be noticed immediately.

It is said that pointed or rough bodies are better "promoters of vaporization" than smooth ones. Make them all alike chemically clean, and they act alike in impeding, rather than promoting, the liberation of vapour. It is true that rough bodies are apt to store up between their furrows or teeth that unclean matter which acts so well as a nucleus. But if a rat's tail file, for example, which is a very active nucleus in its ordinary state, be catharized, either by the action of flame, or of acid and alkaline solutions, it becomes perfectly inactive in a boiling liquid, so far as the liberation of vapour is concerned.

It will be seen that I take no account of the influence of the dissolved air upon the phenomena of boiling, and so far from assigning to it the exalted function of being absolutely necessary to boiling, I doubt whether it has any influence at all, except, in some cases, slightly to diminish the cohesive force of the liquid molecules, but this effect must soon disappear. Water, for example, when cold, dissolves only about $\frac{1}{5}$ th of its volume of oxygen gas, and about $\frac{1}{10}$ th of nitrogen, and these small quantities must be expelled by the heat, and the absorptive power of the boiling liquid for air reduced to a minimum. Can it be supposed that the minute speck of air still left, if it be still left in the boiling liquid, is absolutely necessary for the vapour to expand into, and produce the phenomena of boiling? Can it further be maintained that when bodies act in preventing *soubresauts*, it is by the air they carry down, and that such bodies cease to act as promoters of vaporization when they have discharged all their air? I cannot admit that there is experimental proof for either assertion. A lump of flint that has been exposed to the air, when thrown into a boiling liquid, is instantly covered with bubbles of vapour. Break it into two, and throw in the fragments, not a single bubble of vapour will be seen on the freshly fractured surfaces, but the old surfaces

will be covered as before. If air had anything to do with the matter, the freshly fractured surfaces must have carried down air as well as the old ones. Why then do the new surfaces apparently refuse to act while the old ones are as active as before? We can explain nothing on this theory, but if we say that the freshly fractured surfaces are chemically clean, we can understand why no vapour is given off from them, because there is perfect adhesion between them and the solution as a whole.

There is thus far an identity of action in nuclei, whether as applied to gaseous or saline solutions, or to liquids at or near the boiling point. I have now to invite attention to an extension of the principle of adhesion, consequent on the extension of surface presented by porous bodies. The same force, which, according to Saussure, enables 1 volume of box-wood charcoal to absorb 90 volumes of ammoniacal gas, 85 of hydrochloric acid gas, 65 of sulphurous acid gas, and so on, enables charcoal and some other porous bodies to absorb vapour from boiling liquids, and under the continued action of the heat to give it out in never-ceasing jets, relieving the vessel of all tendency to bumping, making the boiling soft, gentle, and regular, and increasing the quantity of the distillate.

The most remarkable circumstance about this property of charcoal is its untiring activity. No amount of heating, or washing in acid, or alkaline solutions suffices to catharize it. These processes seem rather to improve its strong attraction for gas or vapour in solution. When once in action it will continue for days and weeks together to give off vapour from the boiling liquid, and, unlike the soap, paraffin, &c., used by distillers on the large scale, for the purpose of facilitating the discharge of vapour, the charcoal or other porous body, so far as my experience goes, does not require to be renewed.

In order to show the value of charcoal and other porous bodies in preventing bumping and promoting vaporization, methylated spirit was distilled in a glass retort at a fixed boiling point of 171° F. The distillate collected in five minutes, was weighed and found to be 244 grains. Three or four fragments of charcoal, partly from box-wood and partly from cocoa-nut shell, altogether weighing 20 grains, were now added to the retort, and when the spirit was again fairly boiling, the distillate during five minutes was again collected and weighed. It was now found to amount to 325 grains. The ratio of the results

may be thus stated:—As $244 : 325 :: 100 : 133.2$. Instead of charcoal, 20 grains of pumice-stone in four fragments were next used in the retort, and the ratio of the result was as $100 : 121.7$; with 20 grains of meerschaum—as $100 : 112$; and with 20 grains of coke, as $100 : 107.46$.

These numerical results are, however, very much under-stated, if compared with those obtained in a retort that is structurally free from nuclei, which was by no means the case with the retort actually used. Indeed, it is seldom that we get a retort or a flask, or even a test-tube, that is free from porous specks of ferric oxide or of carbon. These become attached to the glass, while it is still soft in the process of manufacture, and they act as small but powerful nuclei in promoting vaporization and preventing bumping. Indeed, were it not for the presence of these accidental impurities, many a chemical operation must fail from the fracture of the vessel by excessive bumping, and chemists would have only too close an acquaintance with the phenomena of soubresauts. Several writers have noticed that when a liquid is boiled in a glass vessel, the boiling seems to proceed from certain points in preference to others. Donny calls them “foci of vaporization,” and Magnus noticed in the case of an old platinum vessel, containing cracks and scratches, that the vapour was more readily formed at certain points than at others. These phenomena are perfectly explicable on the principle of adhesion on the part of unclean or porous bodies, which, having a stronger attraction for the gases or vapours than for the liquids which hold them in solution, thus effect their separation.

During the last seven years I have applied the principle I am now advocating to the phenomena of the cohesion figures of liquids; to the production of camphor-currents and camphor pulsations; to the motions of creosote on water, and its displacing power with respect to various films; to the adhesion of liquids to liquids; to the curious attractions and repulsions of eugenic acid on water; to the production of tears in the wine-glass, and in solutions; to the production of lightning-figures, which illustrate some new points respecting the disruptive discharge, and the formation of fulgurites; to the effect of clean and unclean surfaces in vegetable nature, such as the different action of the leaves compared with the roots of plants; why dew is formed in globules and not in sheets of water; to certain

phenomena connected with animal and vegetable secretions, and so on. I will now, with your permission, glance at a few other phenomena, which do not seem to me to have been hitherto explained.

I think it was Sir Humphry Davy who found that in attempting to make a voltaic circuit with pairs of plates of metal of the same name, there was no current while the metals were in the same physical condition, but that if one metal of the pair had its surface covered with a film of fatty matter, a feeble current was produced. In such a case the unclean plate separated the gas from the solution, and was thus enabled to perform the part of the conducting plate. So, also, it was found that zinc, tin, iron, and copper, heated in the air until they had become tarnished, were negative towards the bright metals of the same name in acid, alkaline, or saline liquids. In these cases, also, the plates covered with a film had a stronger attraction for the gas of the cell than for the liquid, and thus relieving the cell of gas, were in the condition to act as conducting plates.

A plate of pure zinc is scarcely acted on by dilute sulphuric acid, on account of the perfect adhesion of the acid to the clean surface. Or if gas be liberated when the plate is first immersed, it is from unclean patches or points, but these soon becoming cleansed or catharized by the action of the acid, there is perfect adhesion between the acid and the plate, and chemical action is arrested. The same remark applies to amalgamated zinc, or to impure zinc covered with a film of mercury. The mercury makes the plate chemically clean, and the adhesion of the acid is too close to allow of the escape of gas. Or if gas form when the plate and the acid first meet, the gas goes into solution, and this solution adheres with such force to the plate as to prevent the formation of more gas.

So also in what is called the "passive" condition of iron, and a few other metals in nitric acid of the specific gravity 1.4 to 1.5, the principle of catharism, coupled with the fact that the nitrates of such metals require at least six proportionals of water of crystallisation, which are wanting in the strong acid, seems to me to explain phenomena that have excited an unusual degree of discussion. Gmelin, in his *Handbook of Chemistry* (Cavendish Society's Translation), devotes twenty closely printed pages to the mere analysis of what has been done on

the subject. He says:—"Many metals when immersed in concentrated nitric acid undergo a change; they become more electro-negative, less oxidizable, and lose either wholly, or for the most part, their tendency to decompose acids and metallic saline solutions; they pass from their ordinary *active* state into a *passive* state." Passive iron, for example, will not separate copper from a solution of cupric sulphate or nitrate, nor mercury from mercurous nitrate, nor silver from argentic nitrate, and so on.

Strong nitric acid is so powerful a catharizer that it renders chemically clean an iron wire, however dirty it may be when immersed in it, and the acid adheres to it with such force that it is not readily displaced. I have transferred a bright iron wire from nitric acid of 1·410 sp. gr. to an acid of 1·200 sp. gr., and it has remained for hours in a perfectly passive condition; but if shaken or rubbed beneath the surface of the acid it instantly starts into activity, it changes colour, and a brisk effervescence sets in, with the abundant evolution of red fumes.

In what is called a "pulsating wire" gas is liberated in bursts, separated by intervals of repose. This is similar to what takes place when a glass rod, covered with an oily film, is put into a strong solution of carbonic acid, as in Oersted's experiment. The gas that is liberated from the surface of the wire immediately enters into solution with the adhering acid (which must be diluted to a certain strength, determined by experiment for the wire used). As more gas forms on the surface of the wire, and the acid can hold no more, that first dissolved is driven off with a burst; it accumulates again, again goes into solution, and once more escapes with a burst, and this intermittent action produces the phenomena called pulsation.

The most common case of nucleus is when a body is contaminated with oily, fatty, or greasy matter; but this does not render an iron wire active in strong nitric acid, for such acid immediately acts upon, and displaces the impurity, and catharizes the wire. Iron wire covered with a chemically clean film of oxide, which would be quite inactive in separating a salt or a gas from an aqueous solution, is powerfully active in nitric acid of a certain strength. So, also, if the inactive wire be put into chlorine, or held in the vapour of bromine, or in hydrochloric acid gas, it may be active for a time, at least, if returned to the nitric acid in which it was previously passive. The same

result may be produced by rubbing the passive wire against a softer metal.

I fear I have already exceeded the time allotted to a lecture in this place, but perhaps a few words may be allowed by way of conclusion.

I trust I shall not be assuming too much if I claim for catharism the properties of a principle of nature, namely, generality and breadth of application. The principle is as yet new to science. The work that lies before us in connection with it seems to me to be of importance. I believe that the proper action of nuclei, which this principle teaches, will explain the formation of agates and other siliceous minerals, which is at present obscure. I believe that catharism will account for many, if not for all the cases of increased activity consequent on the nascent state of matter. In that state matter is chemically clean, and hence is endowed with a wonderful activity and power of combination; but no sooner does it emerge from the nascent state, and come into contact with unclean vessels and unclean solutions, than it sinks to the level of activity of ordinary matter. I believe that catharism is competent to explain many of the anomalies connected with ozone, and the increased activity of oxygen at the sea coast, or still better on the wide ocean. I believe that catharism explains why sulphur, phosphorus, and some other bodies sometimes remain liquid during a great length of time at ordinary temperatures; why water may be cooled below the freezing point, as well as many facts in vegetable and animal physiology that are, at present, not well understood. If health and eyesight are spared to me for some time longer, I hope to continue my explorations in this rich field of inquiry; but I shall require time, for my means are very limited, and I have no assistant, or assistance from any one. But if what I have done, am doing, and propose to do, is likely to be in any way conducive to the interests of science, my reward has been already earned.

DISCUSSION.

The President observed that the general conclusion derivable from Mr. Tomlinson's experiments appears to be this:—that there are certain bodies which have the power of causing the liberation of gases or salts from solution, and others which

have not that power; a perfectly clean glass vessel, for example, does not appear to possess this power, but there are certain substances which may overlies its surface, and induce the particular action in question; but we have not yet discovered what it is that causes the separation of one body from another which holds it in solution. Charcoal, even when made perfectly clean, appears to possess this peculiar power in a very high degree.

Dr. W. A. Miller said that Mr. Tomlinson's observations seem to show that the principal agent in producing these singular phenomena is a film of grease, which very generally adheres to the surface of glass vessels and other bodies, and disturbs the balance of adhesion between the solvent and that which it holds in solution. The experiments in question may not have brought us any nearer to the knowledge of the circumstances which cause adhesion between two substances, but they have at least enabled us to advance one step, viz., that of tracing a considerable number of widely scattered phenomena to one very generally operating cause.

Professor Williamson, with reference to the presence of air in liquids during their vaporization, directed attention to the very remarkable observations made some years ago by Mr. Grove,* showing that water, if carefully freed from air and excluded from access of air, may be heated to the boiling point for a very long time without showing any signs of ebullition. We know that every vapour is formed much more readily in presence of a permanent vapour or gas, than when no such gas is present, and though it would be going too far to say that no ebullition can take place without air, we have as yet no evidence that ebullition can take place if permanent gases are completely excluded. The effect of charcoal in facilitating the escape of gases from solutions is decidedly in favour of the view which regards the presence of a permanent gas as necessary to ebullition; for charcoal retains gases within its pores with great tenacity, and even after it has been to a great extent exhausted of air, it probably still retains quantities considerably greater than Mr. Grove found to be contained in the water with which he experimented. With regard to the term "chemically pure," which Mr. Tomlinson uses to distinguish bodies which do not exert this action from those which do, Dr. Williamson said that he felt some difficulty in

* Chem. Soc. J. [2], i, 263.

this application of it, since, to take one example among others, the crystallisation of a supersaturated solution of sodic sulphate is brought about by contact with a crystal of the same salt more certainly and rapidly than by any other substance; now such a crystal cannot well be called chemically impure or unclean.

Dr. Gladstone thought that Mr. Tomlinson's researches had done good service in pointing out the incorrectness of many of the explanations that have been given of the phenomena under consideration, particularly in showing that the smoothness or roughness of a surface has nothing to do with its effect in determining the separation of a gas or of a solid from a solution. This separation appears, according to Mr. Tomlinson, to depend upon the fact that the nucleus or solid substance immersed in the liquid, has a stronger adhesion to the dissolved gas or solid than to the solvent itself. This, however, is not a matter of cleanliness or uncleanness, and, therefore, in speaking of such matters it would be well to get rid altogether of the words "clean" and "unclean." A piece of paraffin may be made perfectly clean, and yet it would certainly produce the effect of removing a salt from solution. Dr. Gladstone also referred to the well known instance of the crystallisation of potassium bitartrate when a potassium salt is mixed with tartaric acid, and the sides of the vessel are rubbed with a glass stirrer, the crystals then forming chiefly on the rubbed portions of the surface; this, again, is a case with which cleanliness or uncleanness has nothing to do. The sudden crystallisation of a supersaturated solution, on dropping into it a crystal of the same salt, appears to depend on the strong tendency which a crystal has to draw to itself other particles of the same substance, in fact, of the tendency of all crystals to grow, and may, therefore, be regarded as affording a strong argument in favour of the general explanation above suggested.

Professor A. Vernon Harcourt objected to the principle of the paper, that it is purely a negative principle, namely, that certain results do not occur in the case of the absence of a number of different substances, that a minute quantity of these substances will produce the results, and that these substances being diffused through the air and in the vessels which we employ are very liable to pass into the solution. The only positive result we could have on the subject would be in the

way of a determination, as suggested by the President, of what kind these substances are which do produce this result. We want to know, for instance, whether charcoal is a substance which produces it in the greatest degree, or whether it is a general property of porous substances, whether it depends upon the evolution of a gas, or what the substances are to which these results are due. Professor Harcourt here referred to a recent observation of his own, which appears to have a bearing upon this subject, although the case is rather an exception to, than an example of, the general fact brought forward by Mr. Tomlinson. In determining the rate of the decomposition of peroxide of hydrogen, he had introduced a measured quantity of dilute solution into glass bulbs, at a certain temperature, and then determined what amount of peroxide of hydrogen remained, hoping so to ascertain what relation the rate of decomposition of the substance bore to the temperature to which it was heated, and the concentration of the solution; but he found some difficulty in making these experiments and obtaining concordant results. Taking exactly the same quantities, being very careful as to the temperature of the solution and the concentration, and, as far as could be observed, having everything in the same way, the quantity of peroxide decomposed after the same length of time was found to differ very much indeed, according to the glass bulbs employed; and the more pains he took in cleaning these bulbs by heating acids in them and by heating alkalis in them, the greater, and not the less, was the amount of decomposition. On examining the matter closely, he observed the very greatest differences between the amount of decomposition, according as he took glass as thoroughly clean as possible, or glass which was not clean. On taking a little oil, and noticing what happened when the bulbs were made dirty in that way, he found that the rate of decomposition was very much reduced indeed; and when the bulbs were varnished over inside, so as to prevent the contact of the glass with the liquid, the decomposition was reduced to a minimum. A dilute solution of peroxide of hydrogen, in a perfectly clean glass bulb, at 70° or 80° centigrade, would be nearly decomposed in half an hour, but would be hardly decomposed in any degree if it was placed in a dirty bulb, or in a bulb varnished inside. Decomposition of the peroxide of hydrogen is very much like the solution of oxygen in water, and the

rate at which the gas is given off in this case seems to be increased by the cleanliness of the glass, and to be diminished when the glass is dirty.

Dr. Odling said that he felt some little difficulty in seeing his way clearly to the conclusion to which Mr. Tomlinson has arrived. This conclusion appears to be that when a liquid containing a gas or crystallisable solid is in contact with a body of a particular kind, the adhesion is not so perfect as in others, and in that case either the gas is evolved or the crystals are thrown down. In the cases where the adhesion is perfect, no gas is evolved and no crystal is thrown down, and if this be the case it becomes a question with which minute division has very little to do. Taking the case, for instance, of the retort, to which Mr. Tomlinson has alluded, we have there two different materials. We have the material which constitutes the great body of the glass, and we have the material which constitutes the nucleus, and under those circumstances it would, perhaps, hardly be a sufficient explanation, to say that the adhesion of the glass is simply less perfect to the nucleus than elsewhere. Supposing we have a retort which is all nucleus, under those circumstances the adhesion will be equal in every direction; nevertheless, there would probably not be any points from which this evolution of gas could take place. Take the case of paraffin which Dr. Gladstone has alluded to. Now, it is a common thing, as Mr. Tomlinson said, to throw grease into water in order to promote ebullition. Suppose we make a retort entirely of paraffin, or one such as Mr. Harcourt has just described, under those circumstances the adhesion of the liquid, however imperfect, will be uniform, and according to Mr. Tomlinson's view, there seems no reason why the ready ebullition of a liquid of low boiling point, due to the non-adhesion to the walls of the paraffin retort, should ever come to an end—why, that is to say, the efficacy of the paraffin or pure grease in promoting ebullition should be temporary only. With regard to the observations of Dr. Williamson, respecting the great difficulty of removing the last traces of air from water, Dr. Odling said that, if he remembered Mr. Grove's experiment accurately, the amount of water given off gradually got less and less up to a certain point, and then there was an almost constant ratio between the amount of vapour given off and the amount of gas, and that ratio continued no

matter how long the ebullition was maintained. Related to this subject, is the fact of many liquids, which nevertheless there is reason to believe are not very absorptive of gas, boiling with very great facility, such bodies as the hydrocarbons, for instance; but it is by no means to be taken as a matter of proof that the quantities of gas retained by a boiling hydrocarbon may not be at least equal to those minute quantities of gas which are capable of being retained by water which has been boiled for a long time. With reference also to the question of charcoal, if it be really the charcoal itself that has this action, the densest and most compact kinds of charcoal ought to answer almost as well as those which are more porous.

Professor Foster said, that he was unable to see in any of the facts brought forward by Mr. Tomlinson, a proof of the incorrectness of De Luc's theory, which supposes that the presence of air or gas of some kind or other is a necessary condition of ebullition. The different effect of a glass rod when it has been exposed to the air, and been carefully cleaned, and the different effects of other bodies under like conditions, seem to resolve themselves simply into different degrees of facility with which they are wetted by the solution into which they are immersed. Now, water cannot wet a body thoroughly unless it is able to displace the air which adheres to the body. If it does displace it, then it wets it, but the greasiness, or whatever may be the condition of the surface, acts, in a great many cases at any rate, by increasing the adhesion of the air, or diminishing the adhesion of the water or liquid, whatever it may be. It is very difficult indeed to form any clear idea of vaporization taking place in the midst of a liquid. If we try to form a definite idea of what the mechanism of vaporization is, we must assume that it consists of such a motion of the particles of the substance, as drives them for an instant out of the sphere of attraction of the neighbouring particles, and, when they once get to a certain distance from them, the attraction of the remaining particles is unable to bring them back again. But if we take Clausius's view of vaporization, or any other equivalent to that, it is impossible to see how any such process could go on in the middle of a mass of liquid; but if we take the smallest quantity of vapour already formed, or gas, or the smallest possible quantity of vacuous space (of course a perfect vacuum would do as well if we could get it), then it is easy to see how

molecules should be driven by the increased action of their neighbours into this space, and liberated once for all from the attraction of their neighbours, and thus appear as gas. Dufour found that liquids of very various character could be heated far above their boiling point, if suspended out of contact either with solid walls to which the gases might adhere, or out of contact with the atmosphere, but that an unfailing way of causing liquids in such a state, when above their boiling-point, to enter into ebullition, was to send an electric current through them. If he had the wires of a battery projecting into the liquid, a globule of liquid heated above its boiling-point, and suspended in some liquid which did not dissolve it, might come into contact with the wire with perfect impunity, but if the battery contact was made so as to make an incipient decomposition, and form a globule of gas, rapid ebullition took place. Professor Foster further stated, that in distilling liquids which one may suppose do not readily dissolve air in very large quantities, for instance, the iodides of methyl and ethyl, he had noticed more than once that ebullition in the distillation of such a liquid ceases completely without the evolution being much slower, evaporation appearing to take place from the surface. All these facts seem to support De Luc's theory, and he could not see that the facts brought forward by Mr. Tomlinson are sufficient to overthrow it.

Mr. Heisch, referring to Mr. Tomlinson's attempt to explain the passive state of iron, by supposing the iron had been rendered perfectly clean by immersion in strong nitric acid, said, we must remember that if we immerse but half an inch of a wire in strong nitric acid, it renders any length of the wire perfectly passive to dilute acid. You may take 50 or 60 feet, and, provided you immerse the end in the strong acid, the whole is rendered passive in the dilute acid, and it is passive only to that same sample. But if you take another vessel and dip the wire into it, the wire immediately becomes active in that vessel, but not in the original nitric acid. Moreover, if you take pieces of iron wire, bend them into a U shape, and place one end in very strong and then in dilute acid, that wire is passive. If you take another vessel, and bring the other end of the U into it, that part is active and dissolves completely. Then take another U, and place one end of it first of all in the

glass in which the iron is being dissolved, and then put the other end of the U into the glass in which it is not being dissolved, and you will find that it is passive at one end and active at the other. But if you reverse the experiment, you make the whole perfectly active. Now, it appears scarcely possible that the fact of the wire being cleaned by the nitric acid can explain these phenomena at all.

Dr. F. Grace Calvert mentioned some remarkable facts relating to the sudden crystallisation of carbolic acid and of glacial acetic acid. Carbolic acid presents in a higher degree than acetic acid the curious property that it may be agitated with a stirrer or anything else, or with dirt—with a solid or not—without undergoing crystallisation. In fact carbolic acid has been known to go all the way from Manchester to the south of France, and reach there perfectly liquid; but on dropping just one crystal of carbolic acid into the liquid, the whole will become a solid mass within the space of perhaps three or four minutes. That is the method which Dr. Calvert constantly adopts in his works, and it affords an instance in which there is not a mere question of a nucleus, or of a solid body determining the formation of crystals. The vessel is far from being chemically clean, the rods which the men use are far from being chemically clean, and yet all this is of no use in causing the liquid to become solid; but just take the most minute quantity, the size of a pin's head, and put it into a vessel where there is 5 cwt. of carbolic acid, and in a moment it will be perfectly solid. The same may be done with acetic acid. You may take a jar of glacial acetic acid, stir it, move it, shake it; but just put a crystal of glacial acetic acid into it, and the whole vesselful, whatever may be its size, will in five minutes be a solid mass.

The President, in calling upon Mr. Tomlinson to reply to the preceding observations, wished to direct his attention particularly—1. To the effect of different conditions of surface in the same body, as in the platinized platinum of Smee's battery, this being a case in which porosity may be supposed to be concerned. 2. To the facilitation of the escape of vapour from boiling water by contact with paraffin, or other greasy matter, which appears to be similar to the case mentioned by Dr. Williamson, inasmuch as we have there a vapour of a different kind, into which the vapour of water can diffuse

itself more readily than into its own vapour. 3. To the question whether these bodies which are called "dirty," have really certain peculiar properties in themselves, and whether if, as Dr. Odling has supposed, they were the containing vessel, they would produce this evolution of gas or induce crystallisation, or whether it is not their presence in contact with another body—whether it is not the dual action—whether it is not the sides of the vessel having a certain amount of attraction for one part of the liquid, and the unclean body for the other, which produces a kind of rending action.

Mr. Tomlinson replied, in substance, as follows:—With regard to the President's observations upon the effect of charcoal in facilitating the evolution of gas, this he could not attribute to the presence of gas in the pores of the charcoal, because after charcoal has been made red-hot and then suddenly quenched under mercury, or plunged into a boiling liquid, it cannot be supposed to retain much air; but by its powerful capillarity, it is always re-absorbing the liquid, and under the continued action of heat, giving it out again. The denser kinds of charcoal act most quickly, because they sink to the bottom of the liquid, and are thus brought nearer to the source of heat. The platinized plates of Smee's battery, Mr. Tomlinson regards as very much in the condition of the plates employed by Davy, exposing them to the air, and getting them oxidized. They collect particles of dust, and get into an unclean condition, and immediately there is a different adhesion between the gas of the cell and the liquid in the cell, and thus there is an easy separation. Interior sides of vessels also are often in a condition of chemical impurity, and it is this difference in adhesive force of a clean and an unclean surface which appears to constitute the whole matter. If a glass rod be exposed to the air, or drawn through the hand or wiped with a cloth, and then put into a solution,—say of soda-water,—it is instantly covered with gas bubbles; the reason of this appears to be that gas will adhere to an oily, greasy, or fatty surface, and water will not. But if the rod be freed from grease, and then put into the soda-water, the solution adheres to it as a whole, and there is no separation, because the adhesion is the same in both cases.

With reference to the phenomena of ebullition alluded to by Dr. Williamson, Mr. Foster and others, Mr. Tomlinson

expressed his opinion that the phenomenon of ebullition, or generally the escape of gas or vapour from a liquid, does not depend on the presence of air in the liquid. In connection with this subject, he referred to two papers which he had published, one in the "Philosophical Magazine," about two years ago, the other in a recent number of the "Proceedings of the Royal Society," in which the following experiments are described:—

A wire cage made chemically clean was lowered into a glass of soda-water, where there was a mass of air surrounded by the solution of carbonic acid, and not a single bubble of gas escaped. But the moment the cage was rubbed between the hands, and then put in, it was covered with carbonic acid. So in the case of a boiling liquid. Several boiling liquids were tried. A wire-gauze cage was lowered, so as to secure a mass of air in the centre, or in the midst of a boiling liquid; and one would suppose that, if the air had anything to do with the liberation of vapour, the vapour would have discharged itself through the meshes of the wire gauze into the cage; but so long as the cage was thoroughly clean, there was no such discharge of steam into the air. But a bit of paper or any solid let fall upon the cage, instantly disengaged large quantities of vapour. From this and a large number of experiments of a similar nature, Mr. Tomlinson infers that nuclei do not act by carrying down air, and that air is not necessary to the ebullition of liquids. In Dufour's experiment referred to by Professor Foster, Mr. Tomlinson considers that the water was in the spheroidal state.

With regard to the sudden crystallisation of a salt or other substance from solution, on dropping into the liquid a particle of the dissolved salt, Mr. Tomlinson concludes from his own observations, that if the crystal be perfectly clean, no such effect takes place; it must be exposed to the air, handled, or otherwise rendered unclean, before it will induce the crystallisation.

NOTE.—In the discussion above reported, several distinguished chemists have objected to the term *catharized* or *chemically clean*, as not embracing all the phenomena. Now, although by far the most common form of impurity is some kind of greasy matter, which renders bodies *unclean*, and therefore *active* as nuclei, while the absence of such fatty matter renders them *clean*, and therefore *passive*, I am nevertheless

bound to admit that cases may arise in which the distinction between *clean* and *unclean* may not apply; as when a solution of a solid in an oil is touched with a bit of ice, both the solution and the ice may be *chemically clean*, and yet the ice may act as a nucleus. So also a supersaturated aqueous solution cannot be kept as such in a vessel of stearin, although such vessel be *chemically clean*. Stearin would act as a nucleus in such a case.

I have already (Phil. Trans., 1868) defined a nucleus as a body that has a stronger adhesion for the thing dissolved than for the liquid which dissolves it.

This differential kind of action is not always expressed, I admit, by such terms as *unclean* and *clean*, unless by an extension of the meaning of such terms as are expressed in the words *a-catharized* and *catharized*; but admitting the definition of a nucleus, as just given, to be correct, the terms *nucleized* and *de-nucleized* would, perhaps, be sufficiently comprehensive to include all cases. Thus, a glass rod which had been exposed to the air, or drawn through the hand, would be *nucleized*, or simply a *nucleus*, as respects aqueous and probably alcoholic solutions, while a glass rod that had been washed in caustic alkali, &c., would be *de-nucleized* or *inactive* as respects such solutions.

The terms *active* and *passive* do not quite accord with my view, since the solutions exert a much stronger adhesive force on a so-called *passive* (clean) as compared with an *active* (unclean) rod.

The principle I advocate is now on its trial. If it be admitted, a correct term will be found for it in the course of examination and further inquiry. I am indifferent as to the name, because I am certain of the reality of the principle.

The other objections that several gentlemen were so good as to bring forward, will be of great assistance to me in enabling me to apply new tests to my work. I propose shortly to reply to them in a separate paper.

C. T.

Highbgate, N., 24th March, 1869.

X.—*On the Butyl Compounds derived from the Butylic Alcohol of Fermentation.*

By ERNEST T. CHAPMAN and MILES H. SMITH.

(Read March 18th, 1869.)

CIRCUMSTANCES placed at our disposal a large quantity of fusel oil,* from which a portion of the amyllic alcohol had been removed. The crude oil, just as it came from the distillers, had been distilled, and everything which came over in one distillation below 127° collected apart. It was this portion boiling below 127° that we operated upon. It had been standing for a good many years in badly-corked jars, and was consequently yellow and dirty. It was saturated with water. We operated on seventeen gallons of this material as follows:—It was first simply distilled, those portions which came over below 115° , and those from 115° to 131° , being collected apart. Everything which came over above 131° was also separately collected. That portion, which came over at 115° — 131° was repeatedly distilled, the distillation being stopped when the thermometer rose to 131° , and that which remained behind being added to that which boiled above 131° . After this process had been repeated about ten times, the greater portion of the liquid boiled between 106° and 115° , or above 131° . That portion which boiled between 115° and 131° was now fractionally distilled in the ordinary manner. It almost entirely split up into liquids boiling above 130° and liquids boiling below 115° . That fraction which originally boiled below 115° was now repeatedly distilled, the distillate being always received in vessels containing freshly-ignited carbonate of potash. This liquid gradually split up into three fractions, the one boiling about 130° , another boiling between 106° and 115° , and the third boiling from 79° up to 106° . This latter fraction was gradually split up into bodies boiling above 106° , and a considerable volume boiling below 80° ; but large quantities remained which no amount of fractional distillation appeared capable of splitting into definite bodies. As will be

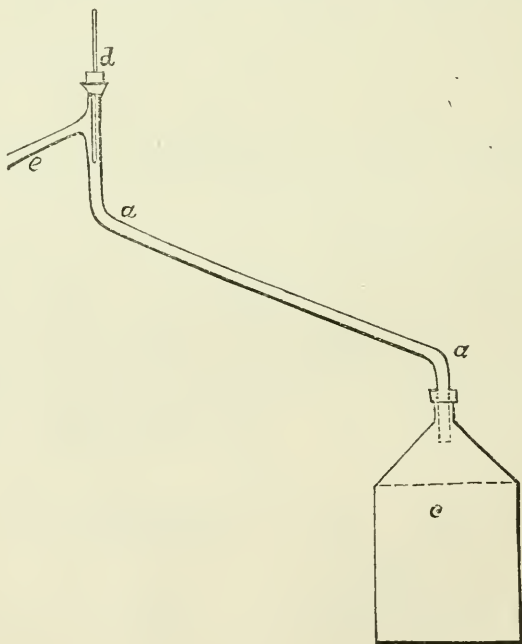
* From London Distilleries.

shown on a future occasion, this portion which proved so unmanageable is of special interest.

The portion boiling between 106° and 115° was now fractionally distilled. We are afraid to say exactly how many times, but the fractionation took up several weeks. Finally, we obtained from it about five litres of a body boiling within some $\frac{3}{10}$ ths of a degree. This substance consists almost entirely of butylic alcohol. It is, however, contaminated with small quantities of iso-butylic alcohol. From this impurity it is impossible to separate it by fractional distillation, notwithstanding the difference in their boiling points.

NOTE.—The fractional distillations were performed in an apparatus like that sketched below.

The distilling vessel consisted of a tin can,* such as is employed for holding methylated spirit or varnish, of two gallons capacity; it could distil conveniently between six and seven litres;



* For the information of foreign readers, we should perhaps remark that in English a *tin can* implies a vessel constructed of thin *sheet iron*, coated with *tin*. It is known in Germany as "*blech*." A small mistake in a foreign translation of one of our papers is the cause of the insertion of this note.

its neck was closed by a cork, through which passed a wide glass tube, bent twice at an obtuse angle.

C is the tin can used as a distilling vessel; *a*, is the tube; *c* is the connection with the condenser, and *d* the thermometer. Of course, great condensation takes place in this long tube, and by slow distillation we may be assured of condensing at least twice as much liquid in the tube as we allow to distil. This condensation very greatly facilitates the separation of the liquids by fractional distillation. The tube employed in most of these operations is about five feet in length, about six-eighths of an inch in internal diameter, at the end connected with the distilling vessel, and rather narrower—say about five-eighths of an inch—at the other end. It is made of very thin glass. We prefer it to a series of bulbs, as recommended by Wurtz, because it exposes a greater amount of surface in proportion to the vapour it contains. Moreover, it more readily drains, is more easily cleaned, and is less fragile. The disadvantage of its inordinate length is, to a great extent, got over by bending it in the manner illustrated.

Butyl compounds may be prepared from the above mixture of constant boiling point. We have prepared and examined in detail the iodide, bromide, nitrate, nitrite, acetate, alcohol and mercury compound.

Iodide of Butyl is a heavy liquid, agreeing accurately with Wurtz's description of it. It cannot be satisfactorily prepared by treating the crude butylic alcohol with iodine and phosphorus; as, under these circumstances, large volumes of butylene are evolved, and a very poor yield is obtained. By operating with hydriodic acid this difficulty is entirely obviated. If the crude alcohol be mixed with a large excess of hydriodic acid of specific gravity about 1.85—1.9, and the mixture be raised to the boiling point, the alcohol is, without sensible loss, converted into iodide.

To prepare the iodide, the crude alcohol is boiled for half an hour or forty minutes with four times its volume of hydriodic acid, of specific gravity about 1.8, or rather higher. At the end of this period the alcohol is completely converted into iodide, which latter will be found to have separated completely from the acid. It is to be separated off, and run into a flask containing carbonate of soda and water. The mixture of crude iodide and carbonate of soda solution is now distilled, and the clear colour-

less iodide separated. It is then dried with chloride of calcium, and fractionally distilled; but by far the greater part of it is found to boil constantly at 121° . Small quantities of liquids of lower boiling point separate out. We prepared altogether about 1,300 grammes of the iodide. The fractional distillation was carried on in an apparatus like that previously described, but consisting entirely of glass. The same remark applies to all other fractional distillations mentioned throughout this paper. Iodide of butyl is a clear, colourless mobile liquid; it boils quite constantly at 121° . Its sp. gr. is 1.6301 at 0° , 1.6032 at 16° , 1.54816 at 50° ; from which it follows that 10,000 volumes at 0° become 10,168 at 16° , and 10,529 at 50° .

The following decompositions of the iodide were observed:—

With alcoholic solution of potash, or ethylate of soda, it is for the most part resolved into butylene and iodide of potassium or sodium, a comparatively small portion only being converted into ethyl-butyl ether.

With alcoholic ammonia it is converted into butylamines, little or no butylene being produced.

Heated with acetate of potash and glacial acetic acid, it is converted into acetate of butyl; a certain amount of butylene is formed at the same time.

Heated with bichloride of mercury, it yields iodide of mercury and chloride of butyl, together with traces of hydrochloric acid and butylene.

On heating it with zinc and ether, large volumes of gas are evolved, and a small quantity of zinc-butyl, which, however, cannot be distilled out of the mixture.

With dilute sodium-amalgam and acetic ether it yields mercury-butyl, not, however, without considerable evolution of gas.

With cyanide of potassium, it yields cyanide of butyl with tolerable facility, and without the liberation of much butylene.

With sodium it yields much gas, consisting in part of butylene and in part of a gas which is, in all probability, hydride of butyl. The radical butyl is produced at the same time, but not apparently in any large quantity.

As will be obvious from the foregoing, this iodide possesses in a high degree the peculiar property of splitting up into hydriodic acid and olefine.

Bromide of Butyl cannot be conveniently obtained by the

action of phosphorus and bromine on the alcohol; partly because much butylene is evolved, and partly because bromous substitution takes place to a very great extent. It is best obtained by saturating the alcohol with gaseous hydrobromic acid, of which it readily absorbs rather less than its own weight. This saturated liquid is to be mixed with its own volume of aqueous hydrobromic acid of sp. gr. about 1.6, or rather less; the mixture is then to be heated in closed vessels up to the boiling point of water.*

The heating must be continued until the oily layer which separates out at the top no longer increases. When this is the case, the digestion vessel must be removed from the hot water, allowed to cool, and opened. The bromide is then separated from the hydrobromic acid by means of the separating funnel. Should it contain phosphorus, as it frequently does (hydrobromic acid frequently having traces of phosphorus adhering to it), it is advisable to wash it with hydrobromic acid, containing a little free bromine. So soon as it is slightly tinged with bromine, it is run into a flask containing a dilute solution of carbonate of soda, and distilled along with that liquid. The distillate is neutral, and perfectly colourless; the oily liquid is separated off from the small quantity of water which accompanies it, and dried over chloride of calcium. It is now fractionally distilled. By far the larger portion boils at 92° C., but another portion which has apparently the composition of bromide of butyl boils 16° or 17° lower. Both liquids distil perfectly without decomposition, and may be separated by fractional distillation, though the process is somewhat tedious.

Bromide of butyl is a colourless liquid of sp. gr. 1.2702 at 16° .

* We employed soda-water bottles, closing them with corks which had been heated in melted spermaceti for half an hour before being used. Corks that have undergone this treatment are readily forced into the necks of the bottles, though beforehand it was impossible to force them in at all. The corks were covered with little tin plates, used by Messrs. Sandford and Blake in securing their soda-water bottles; the corks were wired into the bottles, the tin plates preventing the cork being cut by the wire. The soda-water bottles hold, when full up to the neck, between 270 and 300 c.c., they will therefore take a charge of 200 c.c. conveniently. When charged and wired down, they were placed in tepid water, which was very gradually raised to boiling point. If the temperature be raised too rapidly, the pressure becomes excessive, and there is great danger of the bottles bursting. By raising the temperature gradually, this danger appears to be entirely averted. At least in charging 15 soda-water bottles as above described, not the slightest accident nor even the slightest leakage occurred.

In its reactions, it most closely resembles the iodide, giving off butylene in almost all decompositions. Its reaction with acetate of potash is slow, and requires a tolerably high temperature. At 130° , it takes many hours to complete the reaction, but a little above this point it goes more rapidly.

With sodium amalgam and acetic ether it behaves exactly as the iodide behaves.

With ammonia the same remark applies. With cyanide of potassium decomposition is, perhaps, a trifle slower than with the iodide.

With zinc its behaviour is exactly similar to that of the iodide. It does not appear to react with chloride of mercury. At any rate decomposition is very slow.

With alcoholic potash, it behaves exactly as the iodide does, yielding butylene.

We made about 1,600 grammes of the pure bromide boiling at 92° C.

Nitrate of Butyl.—Nitrate of butyl is a colourless liquid of sp. gr. 1.0384 at 0° , and 1.020 at 16° ; it closely resembles the nitrate of amyl, both in its stability and in its odour, which resembles that of bugs—it boils at 123° . It has the most extremely disagreeable physiological action when inhaled, causing restlessness, and most severe headache. It is prepared by a process strictly analogous to that by which nitrate of amyl was prepared by us. A mixture is made of two volumes of concentrated sulphuric acid, and one of nitric acid of about 1.4 sp. gr., and 100 c.c. of this mixture are placed in a beaker surrounded by salt water and ice. About 30 c.c. of the alcohol are now added from a small dropping funnel, the stem of which is drawn off to a fine point, and passes beneath the surface of the mixed acids; it is employed to stir the mixture, as well as to add the alcohol. The alcohol must be added slowly, and the mixture kept constantly stirred; the nitrate rises to the surface as a clear colourless oil; it is decanted by means of the separating funnel, and run into a retort containing excess of solution of carbonate of soda, the process being repeated until a sufficient quantity of the nitrate has been prepared; then the contents of the retort are distilled. The nitrate passes over quite unaltered along with the vapour of water. It is simply separated from the water, and dried with chloride of calcium. If pure butylic alcohol has been used

in its preparation, it is now chemically pure; if not, it must be fractionally distilled, when but little difficulty will be found in obtaining it of constant boiling point. Nitrate of butyl is unattacked in the cold by concentrated sulphuric acid; very strong aqueous potash has little or no action upon it; alcoholic potash to a great extent resinifies it, but at the same time a small quantity of ethyl-butyl ether appears to be formed: no trace of butylene is liberated, and the action is exceedingly sluggish. The various reactions which we have described in speaking of the nitrate of amyl, may all be repeated with the nitrate of butyl. It is converted into iodide of butyl with great facility when digested with strong hydriodic acid, binoxide of nitrogen, and free iodide being liberated.

Nitrite of Butyl.—Nitrite of butyl is obtained by passing nitrous acid into butylic alcohol; it is very desirable that the nitrous acid should be as free as possible from nitric acid. This may, to a great extent be effected by never heating the mixture of arsenious acid and nitric acid, excepting in the water-bath. Under these circumstances the nitrous acid comes over nearly pure and dry. The butylic alcohol must be kept cool by surrounding it with cold water, and it is advisable to pass the nitrous acid into it slowly. When it is saturated, the passage of nitrous acid must be discontinued, and the nitrite thoroughly washed with water, with dilute caustic potash, and then again with water. It will now present a brilliant bluish-green colour, of which it cannot be deprived by washing; it may be dried over chloride of calcium, and fractionally distilled; the distillate will be yellow. Great volumes of binoxide of nitrogen are evolved during the first portion of the distillation.

Nitrite of butyl is a yellow, light, and very mobile liquid; its boiling point is difficult to determine with accuracy, as it appears to undergo a slight decomposition. However, its boiling point may be taken at 67° ; at least on distilling 120 grammes of it, it began to boil at a little over 65° ; by the time 2 or 3 grammes had passed over, it had arisen to $66\frac{1}{2}^{\circ}$, between which temperature and $67\frac{1}{2}^{\circ}$, almost the whole of the remaining liquid distilled: a very few grammes of liquid remained in the retort by the time the temperature had reached this point. This liquid is almost insoluble in water, and absorbs only the smallest traces of that liquid. It does not dissolve chloride of calcium. Its specific gravity is $\cdot 89445$ at 0° ;

·8771 at 16°; and ·82568 at 50°; therefore 10,000 volumes at 6° become 10,198 at 16°, and 10,833 at 50°. It has the same physiological action that nitrite of amyl has, though the action is more intense. Its smell is not quite so disagreeable. In almost all its decompositions, it closely resembles the before-mentioned nitrite of amyl—thus sodium liberates nitrogen from it; slightly dilute sulphuric acid transforms it into butyrate of butyl, with evolution of binoxide of nitrogen and sulphurous acid. Hydriodic acid converts it into iodide of butyl, with liberation of binoxide of nitrogen and iodine. Ethylate of soda converts it in part into ethyl-butyl ether.

The yield of nitrite of butyl is not very good, unless very great care be taken in its preparation, as the butylic alcohol is easily oxidized into butyric aldehyd and butyric acid, which latter combines with a portion of the butylic alcohol to form butyrate of butyl. Of course the butyric aldehyd is removed during the washing of the nitrite, and the butyrate of butyl during the fractional distillation; 100 parts of butylic alcohol may, however, be made to yield from 105 to 110 of the nitrite.

Acetate of Butyl is prepared by mixing crude butylic alcohol with glacial acetic acid, saturating the mixture with hydrochloric acid, warming in the water-bath, and then washing with cold water. The great bulk of the acetate separates at once; a small quantity, however, remains in the washings, which are therefore distilled; the distillate is treated with carbonate of potash; and the oily layer separated from the aqueous one. The oily layer is again treated with glacial acetic acid and hydrochloric acid, and washed as before. The acetate so recovered is about 10 per cent. of the whole preparation. The mixture is now carefully dried, first by agitation with carbonate of potash, and subsequently by long standing over a new portion of the freshly ignited carbonate. It is now carefully fractionally distilled. Notwithstanding the drying, the first portions of the distillate are always a little wet; they are therefore received in a flask containing more ignited carbonate. Other compounds of lower boiling point than the acetate, separate from it during the distillation. Acetate of butyl boils at 117·5. Its sp. gr. is ·89096 at 0°, ·8747 at 16°, and ·83143 at 50°. Therefore 10,000 volumes at 0° become 10,186 at 16°, and 10,716 at 50°. The smell of the acetate is fragrant, only

distantly resembling that of acetate of amyl; it recalls the odour of quince. It is not easily decomposed by treatment with aqueous caustic potash. By sealing up, however, and so raising the temperature to 140° decomposition takes place very rapidly. With strong aqueous ammonia the ether is slowly decomposed into acetamide and butylic alcohol. With alcoholic potash, it is decomposed almost instantaneously. With solution of potash in butylic alcohol, the decomposition is equally rapid.

Sodium dissolves in the acetate absolutely without evolution of gas.

Butylic Alcohol.—The pure alcohol is most readily obtained by decomposing the pure acetate with caustic soda. The acetate is poured upon about half its weight of powdered caustic soda. After a few minutes the mixture gets hot, and finally boils violently. It should now be cooled by immersing the vessel containing it in cold water. The mixture will now have become a semi-solid mass. Water is now to be added, and the whole distilled from the oil-bath. Butylic alcohol accompanied by acetate of butyl and water, distil over.

The distillate is now saturated with carbonate of potash, the oily portion decanted, and treated as before with caustic soda. In this second operation, the conversion into the alcohol is quite complete. The mixture is now treated with water, and again distilled from the oil-bath; the distillate treated with carbonate of potash as before, then thoroughly dried by boiling with and allowing to cool over carbonate of potash. It is next treated with a large quantity of caustic lime, over which it must either be allowed to stand for some weeks, or else it must be digested along with the lime at a temperature between 65° and 75° for 12 or 14 hours. On now distilling it off the lime in the oil-bath, it will be found to be perfectly dry. It boils at $108\frac{1}{2}^{\circ}$ at the normal pressure, going *quite* to dryness below 109° . Its specific gravity is .8055 at 16° . Its smell is quite different from that of the alcohol, with a trace of moisture in it.

Butylic alcohol cannot be dried by treatment with sodium. It would appear that hydrated oxide of sodium is more or less decomposed by butylic alcohol, water and butylate of sodium being the products. At any rate, butylic alcohol, dried as perfectly as possible with carbonate of potash, was not rendered anhydrous by treatment with 6 per cent. of sodium. This

alcohol could not have contained much over 1 per cent. of water, so that there was much more than sufficient sodium to form even anhydrous oxide of sodium with the oxygen of all the water present.

When quite dry, butylic alcohol will dissolve about half an equivalent of sodium, though only with considerable difficulty, and with the aid of much agitating and heating. Butylic alcohol readily dissolves chloride of calcium, acetate of potash, and caustic potash. It does not appear to dissolve notable quantities of the chlorides, nitrates or sulphates of the alkalies. It does not dissolve cyanide of potassium. It is readily miscible with glacial acetic acid, also with glacial acetic acid to which twice its volume of water has been added. It is very readily soluble in hydrochloric acid. It dissolves in about 11 volumes of water. If large volumes of the alcohol be distilled, it is possible to obtain a portion of it nearly, if not quite anhydrous. The best plan of drying really large volumes of the alcohol appears to be, to distil it repeatedly, always treating the first portion of the distillate with carbonate of potash. The alcohol appears to form a definite hydrate, which, however, cannot exist at the boiling point of water. Treated with iodide of phosphorus, or iodine and phosphorus, the alcohol is converted partially into butylene, and partially into iodide of butyl. We have never been able to obtain a conversion of more than 60 per cent. of the alcohol into the iodide. With bromine and phosphorus a perfectly similar decomposition takes place. If the alcohol be cooled to -15° or -16° C., and then poured slowly into concentrated sulphuric acid kept at the same low temperature, the alcohol appears to be totally, or almost totally converted into butyl-sulphuric acid. If the mixture be effected at the ordinary temperature, polymerised butylene appears to be the principal product. If the sulphuric acid be diluted with a third of its weight of water, and the mixture gradually effected at the common temperature, butyl-sulphuric acid is the principal product. If butyl-sulphuric acid be diluted and gently warmed, and excess of crystallised sulphate of soda added, a colourless liquid, of most extraordinary odour, rises to the surface. This liquid is soluble in water in all proportions. It appears to be a hydrate of butylic alcohol. At any rate, on distillation, it splits up into water and butylic alcohol.

Mercury-Butyl.—Mercury-butyl is easily prepared by the

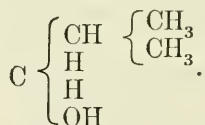
general method given by Frankland and Duppa for the preparation of the mercury-compounds of the alcohol radicals. Five grammes of sodium were dissolved in over 2,000 grammes of mercury, and agitated with an equivalent quantity of iodide of butyl, to which about one-tenth of its weight of acetic ether had been added. The process was carried on in a stout glass-stoppered bottle, the stopper of which was removed and its place supplied by a bored cork carrying a long, wide, upright, glass tube; this served as a condenser. When the mixture in the bottle was vigorously shaken, the mercury, which at first remained fluid, soon divided itself into an infinite number of minute globules, which, with the liquid and iodide of sodium, formed a grey, pasty mass, in which, after a while, not a single globule of mercury could be discovered. On further agitating the mixture, as the reaction slackened, the mercury coalesced again into a liquid mass. Great heat was given out during the reaction. When the bottle was nearly cold, it was found that the mercury could be poured out in a perfectly clean state, without the smallest difficulty, the whole of the mercury-butyl, iodide of butyl, &c., remaining in the form of a paste, along with the iodide of sodium formed, and a small quantity of mercury. The mercury was at once re-amalgamated, poured into a clean bottle, and again treated with iodide of butyl and acetic ether, as before. During the progress of the second operation, the first bottle was washed out, the washings being collected in a retort; this bottle was now dried and was ready to receive the charge of mercury from the other bottle by the time the operation going on in it was completed. The process was continued in this way until a sufficient quantity of crude mercury-butyl had been obtained.

The contents of the receiving retort consisted of two layers, an aqueous layer, and a layer of dense liquid at the bottom. Most of the water in the retort was removed, and the contents of the retort were distilled from the oil-bath. Mercury-butyl passes over readily with the vapour of water. The distillate consisted of two very well-defined layers, the lower being mercury-butyl contaminated with iodide of butyl and acetic ether. To free it from these two latter impurities, it was placed in small retorts, and a current of steam driven through it; this was continued until no iodine could be detected in the distillate. The liquid in the retort was now separated from the water accompanying it, and dried with chloride of calcium.

Mercury-butyl thus prepared, is a colourless, transparent liquid, of sp. gr. 1.7469 at 0°, and 1.7192 at 16°. It cannot be distilled by itself, but it will stand a temperature of 130° without undergoing much decomposition. It combines with iodine and bromine with characteristic violence. Boiled with hydrochloric acid, it liberates a gas, apparently hydride of butyl. It is attacked with comparative facility by zinc, forming zinc-butyl; no great disengagement of gas takes place in the transference.

It has the peculiar disagreeable, yet perfume-like smell, which appears to be characteristic of the whole of this class of bodies, but we did not experience the slightest ill effects from working with it. Its smell is one, the dislike to which is soon converted into absolute disgust. We are not acquainted with any substance, excepting these mercury-radicals, the smell of which we cannot more or less accustom ourselves to; but though at first the smell does not strike one as being peculiarly disagreeable, after a few days' work we seemed instinctively to shrink from it; we have prepared all the known mercury-compounds of the alcohol radicals, and have always found that they produce this extreme disgust. We may here observe, that we do not think that there is any great danger in working with these compounds now that their poisonous nature is so well established.

The butyl spoken of in the above paper, is isopropyl-methyl; the alcohol, therefore, would be, in Kolbe's nomenclature, isopropyl carbinol, and is represented by the formula—



The alcohol yields on oxidation, iso-butyric acid. We defer a detailed account of its oxidation products to a future communication.

The following is a tabular statement of the boiling-points and specific gravities of those butyl-compounds examined both by Wurtz and ourselves.

With regard to the specific gravity of the iodide, we have here inserted a specific gravity observed at 19°, so that the numbers may be strictly comparable. It will be seen that whilst

the iodide and alcohol agree closely as to boiling-point, all the other compounds differ notably. As we have made many preparations of all these compounds, and have operated on a very large scale, we think the numbers we give may be implicitly depended upon:—

Name of substance.	Boiling point C°.		Specific gravity.	
	Wurtz.	C. & S.	Wurtz.	C. & S.
Iodide of butyl.....	121	121	1.604 at 19° C.	1.593 at 19° C.
Bromide of ditto.....	89	92	1.274 at 16° C.	1.2702 at 16° C.
Nitrate of ditto	130	123	heavier than water	1.020 at 16° C.
Acetate of ditto	114	117.5	.8845 at 16° C.	.8747 at 16° C.
Butylic alcohol.....	109	103.5	.8032 at 18.5° C.	.804 at 18.5° C.

APPENDIX,

Containing the evidence on which the above account of the butyl-compounds rests.

A. The following is the proof on which we base our assertion that we are dealing with butyl-compounds:

First. A combustion of the alcohol. Burnt with chromate of lead. .3507 grammes of the alcohol yielded .8348 grammes of carbonic acid and .440 grammes of water, from which the following percentages of carbon and hydrogen are calculated:—

		Theory.
C ₄	64.92	64.87
H ₁₀	13.94	13.51
O		21.62

Second. A combustion of the iodide obtained from the alcohol was made. Burnt with chromate of lead and copper-turnings, .844 grammes of the iodide yielded .807 grammes of carbonic acid and .3775 of water. These iodine determinations were made in three different samples of the iodide prepared at different times.

I. 1.257 grammes of the iodide yielded 1.6016 of iodide of silver. II. .6904 of iodide yielded .8839 of iodide of silver. III. .8830 of iodide yielded 1.1253 of iodide of silver.

From the above, the following percentages are calculated:—

		I.	II.	III.
C	26·08	—	—	—
H	4·97	—	—	—
I	—	68·86	69·19	68·87

		Theory.	Found.
C ₄	48	26·09	26·08
H ₉	9	4·89	4·97
I	127	69·02	68·97 (mean)
	<hr/>	<hr/>	<hr/>
	184	100·	100·02

These iodine determinations were made by decomposing the iodide with alcoholic soda free from chlorine (obtained by dissolving sodium in alcohol). The alkaline iodide was rendered acid by dilute nitric acid and precipitated with nitrate of silver.

The iodide of butyl was also titrated in the manner described by Professor Wanklyn, the digestion being carried on in sealed tubes.

I. 2·471 grammes of iodide digested with alcoholic soda, neutralized as much alkali as 13·5 c.c. standard sulphuric acid would have done.

II. 5·384 grammes of iodide neutralized soda, equivalent to 29·3 c.c. of standard acid.

These titrations correspond to the following percentages of iodine:—

I. 69·38 II. 69·11 Theory, 69·02.

When we recollect that the atomic weights of propyl, butyl, and amyl are as follows, C₃H₇ = 43, C₄H₉ = 57 and C₅H₁₁ = 71, we see that a determination of the atomic weight at once points out with which radical we are dealing. Now the atomic weights as deduced from the three iodine determinations are respectively:—

I. 57·43; II. 56·55; III. 57·4.

The atomic weights deduced from the titrations are—

I. 56·05; II. 56·76.

The above appears to us to be ample, and more than ample, proof that we were dealing with butyl compounds; incidentally, it establishes also the purity of the alcohol and the iodide.

B. *Proof of Purity of the Iodide of Butyl.*—This depends, 1st,

on the combustion given above; 2nd, on the three iodine determinations given above; 3rd, on the two titrations given above; 4th, on the yield of iodide from the alcohol. 80 grammes of the alcohol were digested with a very large excess (500 cc.) of hydriodic acid of specific gravity 1·8, for forty minutes. The mixture was then distilled, the distillate rendered alkaline with carbonate of soda, and again distilled. The heavy oily layer of the distillate was pipetted off, and while still wet, weighed. Weight, 198·5 grammes. To ascertain how much water hung about it, 200 grammes of the pure dry iodide were distilled from carbonate of soda solution, and the distillate weighed, &c., as before; it now weighed between 201·5 and 201·6. We may, therefore, assume that the increase of weight due to moisture was about 1·5; this gives us 197 grammes as the yield of iodide from 80 grammes of alcohol, therefore—

100 parts of alcohol yield 246·25 parts of iodide.

100 parts of butylic alcohol yield 248·65 parts (theoretically.)

100 parts of propylic alcohol yield 283·33 parts (theoretically.)

100 parts of amylic alcohol yield 225 parts of iodide (theoretically.)

We have, therefore, obtained 99·03 per cent. of the yield of iodide theoretically obtainable from butylic alcohol.

C. *Proof of purity of Bromide of Butyl.*—This rests entirely on the yield, under the circumstances a perfectly sufficient datum. Two experiments were made on 80 grammes of the alcohol.

I. yielded 147·4 grammes of bromide; II. yielded 146·7 grammes; or, calculating from these yields—

By I., 100 parts of alcohol yield 184·25 of bromide.

„ II., „ „ „ 183·38 „

Theoretically „ „ 185·14 of bromide of butyl.

We have, therefore, obtained respectively—

I., 99·52 per cent.; II., 99·05 per cent. of the theoretical yield.

The conversion of the alcohol into the bromide was effected in soda-water bottles. The weighing of the bromide was in this instance effected dry; the contents of the soda-water bottles were distilled, the distillate re-distilled from carbonate of soda solution, the oily layer pipetted off, and dried over chloride of calcium; it was now decanted from the chloride of calcium, and weighed. Water was now added to the chloride of calcium, and the mixture distilled, whereby a few grammes

of bromide were recovered; these were decanted and weighed wet, and their weight added to the weight of the dry bromide. As in neither case did the weight of this wet portion amount to 4 grammes, and as bromide of butyl does not contain more than .7 per cent. of water, the error introduced by weighing this bromide wet could never amount to 0.03 grammes, a quantity totally without influence on the result, and indeed only influencing a figure in the third or fourth decimal place.

D. *Proof of purity of Nitrate of Butyl.*—This depends also on the yield. From the nature of the method of preparation, a very sharp result could not be expected. Two determinations were made:—

I. 80 grammes of the alcohol yielded 126.5 grammes of the nitrate.

II. 100 grammes of the alcohol yielded 158.5 grammes of the nitrate.

Calculating from I., 100 parts of the alcohol yield 158.13 of the nitrate; and by II., 100 parts of the alcohol yield 158.5 of the nitrate. Theoretically, 100 parts should yield 160.8. From I., therefore, we have obtained 98.35 per cent. of the theoretical quantity, and from II., 98.57 per cent.

E. *Proof of purity of Acetate of Butyl.*—In this case we could not depend upon the yield, because it is necessary to wash the acetate many times, and because it is difficult to ensure the total conversion of the alcohol into the acetate. Still, by distilling the washings, and treating the mixture of acetate and alcohol obtained from them with glacial acetic and gaseous hydrochloric acids, and again separating the acetate so obtained, we succeeded in obtaining between 96 and 97 per cent. of the theoretical yield. The proof of the purity of the acetate, however, rests on titrations, of which two were made.

I. 3.9246 grammes of acetate neutralized as much caustic potash as 42.2 c.c. of standard acid could have done.

II. 4.9846 grammes neutralized as much potash as 53.7 c.c. standard acid; of this acid 1 c.c. equals 0.03118 grammes of potassium. From these numbers we calculate that, according to—

I. It yields 51.44 per cent. of acetic acid; and according to II., 51.53. Theoretically, it should yield 51.72.

F. *Proof of purity of Mercury Butyl.*—This rests on a determination of the mercury contained in the compound.

0.370 of the compound yielded 0.235 of metallic mercury,

therefore 63.51 per cent.

Theory for $(C_4 H_9)_2 Hg$ requires

63.69 „

G. *Proof of purity of Butylic Alcohol.*—This rests first on the combustion quoted above; secondly, on the yields of iodide, bromide, and nitrate; lastly, on the purity of the numerous butyl compounds obtained from it, as shown by the iodine determinations and other analyses quoted above.

H. The annexed table contains the equivalent of butyl deduced from the various analyses mentioned above. It is appended chiefly because in this manner, and in this manner only, can the exact comparative value of the different estimations be seen, since the intervals between the percentage composition of different compounds vary so greatly, that what is a sufficient approximation to the truth in one case, has comparatively little meaning in another; thus, in comparing one combustion with another, for example, a combustion of butylic alcohol with one of iodide of butyl, an error of 0.25 per cent. in the carbon, in the case of the alcohol, would only correspond to an error of 0.1 per cent. of carbon in the iodide. If, therefore, we were to argue from two combustions, one of the alcohol with an error of .5 per cent., and one of the iodide with an error of .25 per cent., we should arrive at a more accurate result by using that combustion with the largest apparent error.

TABLE showing the Atomic Weight of Butyl, as deduced from the following 13 determinations.

Nature of Determination.	Atomic weights deduced from,	
	Sets of Experiments.	Isolated Experiments and means of sets.
(1.) By combustion of alcohol, C + H found = 79.86 per cent. 100 - (C + H) found 22.14. 22.14 : 79.86 :: 16 = (Eq O) : atomic weight.....	..	56.27
(2.) By combustion of iodide, C + H found = 31.05 per cent. 100 - 31.05 per cent. = 68.95 ∴ 68.95 : 31.5 :: 12.7 = (Eq I) :	57.19

Nature of Determination.	Atomic weights deduced from.	
	Sets of Experiments.	Isolated Experiments and means of sets.
By estimation of iodine in iodide as Ag I—		
(3.) I.	57.43	
(4.) II.	56.55	
(5.) III.	57.40	
Mean	57.13
By estimation of iodine in iodide by titration—		
(6.) I.	56.05	
(7.) II.	56.76	
Mean	56.41
(8.) By yield of iodide of butyl from alcohol	58.22*
By yield of bromide—		
(9.) I.	57.77	
(10.) II.	58.56	
Mean	58.17
By titration of acetate—		
(11.) I.	57.64	
(12.) II.	57.42	
Mean	57.53
(13.) By estimation of Hg in mercury butyl.	57.46
Mean of all determinations	57.30

DISCUSSION.

Dr. Odling objected to the definitions commonly given, especially in text-books, of primary, secondary, and tertiary alcohols, these definitions being based upon the manner in which the carbon atoms are supposed to be grouped, whereas it would be much better that they should be founded upon reactions. The definition of a body should, in fact, be that it is one which behaves in a particular way, from which its constitution is afterwards inferred. Thus with regard to the particular case under consideration, an alcohol may be classed as primary, when it

* We should perhaps here point out that the method of exhibiting the results of analysis in atomic weights, whilst it shows the relative value of analyses better than any other plan, exaggerates the apparent error very much. Thus, for example, if we exhibit the percentage composition of iodide of butyl as determined by the yield, we obtain 68.57 per cent. of iodine, a result which is $\frac{6.5}{10000}$ of the iodine in error, but the atomic weight is 58.22, a result $\frac{2.4}{10000}$ in error.

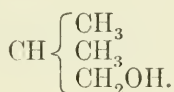
yields by oxidation an acid containing the same number of carbon atoms.

Hydrocarbons may be formulated first, according to the residues which they contain, viz.:—

Methyl.....	CH ₃ '.
Methylene	CH ₂ ''.
Formyl	CH'''.
Carbon	C''''.

Secondly, according to the number of each of these constituent residues; and, thirdly, according to the manner in which they are tied together.

The hydrocarbon C₄H₁₀, from which the butylic alcohol under consideration is derived, is admitted to contain the residue CH₃ three times, its formula being CH(CH₃)₃, and the primary alcohol derived from it by substitution of OH for H in one of the groups, CH₃ will be—



Such formulæ have this advantage over those now generally in use, that they do not involve any particular assumptions as to the superiority in importance of one hydrocarbon residue over another, and its consequent selection for the post of honour as the typical basis of the formula.

Professor Wanklyn said that the classification of alcohols according to the linking of the carbon atoms, appeared to him to be indirectly a classification according to reactions, but that he preferred to classify according to the linking, and to have criteria by which to recognize that linking. The butyl alcohol which forms the subject of Mr. Chapman's paper, is a primary alcohol, that is an alcohol in which the carbon, which is united with hydroxyi, is united directly with only one atom of carbon. The criterion by which we recognize such an alcohol is that by oxidation it gives an acid containing the same number of atoms of carbon as the alcohol itself. The alcohol that Mr. Chapman has examined fulfils this character. By oxidation it gives isobutyric acid, which has the same number of atoms of carbon as the alcohol. In order to get this isobutyric acid, we have to oxidize carefully, but still we *can* get an acid containing the

same number of atoms of carbon as the alcohol. This alcohol would be called a *pseudo-primary*, or an *iso-primary alcohol*. The proof that this alcohol is not the normal butylic alcohol

C $\begin{cases} \text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{H}_2 \\ \text{OH} \end{cases}$, is that the four-carbon acid formed from it by

oxidation is not common butyric acid C $\begin{cases} \text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{O} \\ \text{OH} \end{cases}$, but iso-

butyric acid C $\begin{cases} \text{CH}(\text{CH}_3)_2 \\ \text{O} \\ \text{OH} \end{cases}$, identical with that which is produced

by the action of alkalies on cyanide of isopropyl. The salts of these two acids exhibit considerable diversities of character. The calcium salt of isobutyric acid is much more soluble than ordinary butyrate of calcium, and isobutyric ether boils at 112° , whereas butyric ether boils at 119° .

Mr. Chapman observed that a further difference between these two isomeric acids is afforded by the fact that isobutyric acid breaks up on oxidation, whereas normal butyric acid does not.

Dr. Odling said that it was not the ordinary mode of classifying the alcohols that he objected to, but the definitions. He thought, as a matter of logic, that the definition should have reference, as nearly as possible, to the criteria or characteristic properties of bodies, so that in saying that a body belongs to a particular class, we should be understood as implying that it behaves in a particular way.

Dr. Crum Brown said that he perfectly agreed with the last remarks that had fallen from Dr. Odling, though he could not quite agree with him respecting the classification of the alcohols. Some alcohols when oxidized yield an aldehyde, and some aldehydes (those namely to which the term is generally applied) yield by oxidation acids containing the same number of carbon atoms. Now, the alcohols which yield aldehydes converted by oxidation into the corresponding acids, are those which we call primary alcohols. Then, again, there are alcohols convertible by oxidation into aldehydes (ketones) which, when subjected to the action of oxidizing agents, split up into two acids; these are the secondary alcohols. And, lastly, there are alcohols which do not yield aldehydes at all, but split up at once by oxidation into acids containing smaller num-

bers of carbon atoms. So far as we can at present see, from observed facts, primary, secondary, or tertiary alcohol is a carbinol in which 1, 2, or 3 atoms of hydrogen are replaced by alcohol radicals. By classifying in this way we get rid of the danger attending the too free use of the atomicity theory, which must be regarded as at best only a temporary expedient, destined sooner or later to be replaced by a theory more in accordance with the true principles of physics. Theories, in fact, are but mere scaffolding; let them be used as such, and knocked away when the proper time comes.

Dr. Guthrie inquired what was the precise origin of the fusel oil upon which Mr. Chapman had been working. It would be interesting to know whether it was obtained from potatoe spirit or grain spirit.

Mr. Chapman expressed his regret at not being able to give an exact answer to the question, and, indeed, he thought it would be difficult to obtain a precise answer, as many distillers are in the habit of using mixed grains. The fusel oil upon which he had worked was obtained from Bowerbank's and from Whatney's, and, unfortunately, the two had been mixed before he got them. He had, however, examined many other specimens of fusel oil, and they all appeared to contain butylic alcohol.

Returning to the question of formulæ and classification, Mr. Chapman said: "I do not see any objection to the mode of defining the several classes of alcohols proposed by Dr. Odling and Dr. Crum Brown, which, indeed, is quite in accordance with observed facts. There is, however, one cardinal point about alcohols or the compounds derived from them. Some alcohols split up directly into olefine and water, and some do not. Now, can we not base some kind of classification upon this fact, or can we not make it a portion of some classification? I, of course, have never seen what would be called normal primary butylic alcohol. But if it should turn out that on treating normal iodide of butyl with alcoholic potash, no butylene whatsoever is evolved, and that on treating this isopropyl carbinol with alcoholic potash, butylene is evolved, as we know it is, I think we should there have a very fair ground for beginning to make a very wide division of the alcohols, and that we should, perhaps, be justified in calling one set of them hydrates of olefines, and another alcohols, giving them two generic names. There

is, however, another question not immediately connected with this. Before we can argue very directly, as Dr. Odling and Dr. Crum Brown appear to wish, from the reaction to the nomenclature, we must have a very much more careful study of the reactions than has hitherto been made. At the present moment we do not know whether, on treating iodide of amyl with alcoholic potash, any amylene is evolved or not, or whether on treating common iodide of ethyl with alcoholic potash any ethylene is evolved. I have, however, ascertained that on treating normal bromide of propyl, which I have obtained from another portion of this fusel-oil, with alcoholic potash, no olefine, or only an infinitesimal quantity, is evolved."

XI.—On a certain Reaction of Quinine.

By Professor G. G. STOKES, F.R.S.

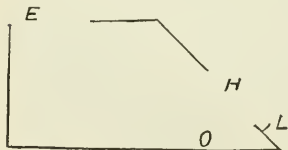
(Read March 18th, 1869.)

In the course of two papers on optical subjects, published in the Philosophical Transactions, I have mentioned a peculiar reaction of quinine having relation to its fluorescence.* About that time I followed out the subject further, and obtained results which were interesting to myself, especially in relation to a classification of acids which they seemed to afford. Not being a chemist, I did not venture to lay the results before the chemical world. I have, however, recently been encouraged by a chemical friend to think that a further statement of the results might prove of some interest to chemists.

The reaction is best observed by diffused daylight entering a darkened room† through a hole in the shutter, which may be

* Phil. Trans. for 1852, p. 541, and for 1853, p. 394.

† In default of a darkened room, a common box, such as an old packing-case, may be readily altered so as to answer very well. The box is sawn obliquely across, the cutting plane being parallel to one edge, as indicated by the figure, which denotes a vertical section. The aperture thus made is covered by a board nailed on, containing a hole, H, destined to be covered by the glass plate, which is kept from slipping down by a small ledge, L. A portion of the upper covering of the box at E is removed to allow the observer to see and mani-



four or five inches square, and which is covered with a deep violet glass, coloured by manganese.* In front of the hole is placed a white porcelain tablet, or else one of the porcelain slabs with shallow depressions used for colour tests. A solution of quinine in very weak alcohol is strong enough for the observations, or else very minute fragments may be used. In some cases, as for example with valerianic or benzoic acid, the presence of alcohol interferes with the reaction.

It will conduce to brevity and clearness to describe in the first instance, in a little detail, the phenomena exhibited by two particular acids, say sulphuric and hydrochloric.

Let a series of drops of the quinine solution be deposited on the porcelain. If one of these be touched by a rod dipped in dilute sulphuric acid, the beautiful fluorescence of the quinine is instantly developed. If another drop be similarly touched by a rod moistened with dilute hydrochloric acid, no apparent effect is produced.† Nor is this all. If a little hydrochloric acid be introduced by a moistened rod into the fluorescing drop, the fluorescence is immediately destroyed. If a little of the sulphuric acid be introduced into the drop containing only hydrochloric acid, no effect is produced.‡

If a series of drops of a solution of quinine in dilute sulphuric acid be deposited, and a little solution of chloride of potassium, sodium, or ammonium be added, the fluorescence is immediately

pulate. In observing, the box is placed near a window, with its slant side turned towards the light; the hole is covered with its glass; the object is placed at O; and the observer looks in through E, covering his head with a dark cloth, to exclude stray light.

* Flint glasses answer best, the colour given by manganese to crown glass being generally somewhat brownish. I have, however, seen one specimen of crown glass coloured by manganese, the colour of which was as fine a purple as that of the flint glasses.

† It is true that a solution of quinine in dilute hydrochloric acid is fluorescent, and with concentrated sunlight, or with sunlight uncondensed, but analysed by absorption or dispersion, the fluorescence comes out strongly. It is, however, notably inferior to that produced by sulphuric acid; and for our immediate object a mode of observation in which it hardly, if at all, appears, is even better than one adapted to bring out comparatively feeble degrees of fluorescence. When I speak in the text of fluorescence being *destroyed*, the expression must be understood in this qualified sense.

‡ It must be understood that I am not here dealing with concentrated acids, nor with any very great preponderance of one kind over another. I suppose all the solutions to be dilute, and the quantity of acid employed, of whatever kind, to be many times that merely required to combine with the quinine.

destroyed. The action of sulphate of potassium, &c., on a solution of quinine in water acidulated, whether with hydrochloric or sulphuric acid, is in each case merely negative.†

Now, on trying a variety of acids, I found that with hardly an exception, unless when the acid character of the acid was only indistinct, the acids ranged themselves with perfect definiteness into two classes, which I will call class A and class B. Those of class A developed fluorescence in a solution of quinine in water just like sulphuric acid, the amount of fluorescence being comparable with that produced with sulphuric acid, and the tint the same. Those of class B not only did not produce it, but destroyed it when produced by acids of the class A. This destruction is produced by the alkaline salts of the acids, as well as by the free acids themselves, and thus we are able to classify acids without having specimens of the free acids at hand.

In the following lists, those acids which were tried only indirectly, by means of one or more of their alkaline salts, are distinguished by an asterisk:—

Class A.	Class B.
Acetic	Hydriodic*
Arsenic	Hydrobromic*
Benzoic	Hydrochloric
Chloric	Hydroferrocyanic*
Citric	Hydropalladiocyanic*
Formic	Hydroplatinocyanic*
Hyposulphuric*	Hydrosulphocyanic*
Iodic	Hyposulphurous*
Malic	
Nitric	
Oxalic	
Perchloric	
Phosphoric	
Silico-fluoric	
Succinic	
Sulphuric	
Tartaric	
Valerianic	

† See the preceding note.

Unless a quinine solution be sufficiently dilute, when alcohol is used, iodic acid produces a precipitate. In what precedes, it must be understood that I refer in all cases to solutions. The character of the fluorescence of the salts of quinine in the solid state varies from salt to salt. The solid iodate obtained by precipitation is strongly fluorescent, with a blue considerably deeper than that of the solutions.

It is not in all cases possible to try all the reactions stated to belong to the acids above mentioned. Thus, in the case of iodic acid, the solution cannot be tested by ferrocyanide of potassium, which instantly decomposes the iodic acid. But the strong fluorescence of the iodic solution, and the immediate destruction of the fluorescence by chloride of sodium, &c., alone suffice to show definitely to which class iodic acid belongs.

The absorption of the fluorogenic* rays by the yellow ferrocyanide of potassium, would itself alone account for the apparent destruction of the fluorescence *if the salt were present in sufficient quantity*. Actually, however, the quantity which suffices to destroy the fluorescence is much less than what would be required to prevent its exhibition by the absorption either of the fluorogenic or of the fluorescent rays, or of both. When the experiment is properly tried, there cannot be a moment's hesitation that the removal of the fluorescence is a true chemical reaction, and not a mere optical effect. This may be further proved by spreading a comparatively large quantity of the ferrocyanide solution in the form of a broad drop on glass, and holding it immediately over the gleaming drop of the quinine solution, when, though the fluorogenic rays entering, and the fluorescent rays leaving the drop, have both to pass through the whole thickness of the absorbing solution, the fluorescence observed is only somewhat reduced. The absorption of the fluorescent rays in this case goes indeed for little; it is the absorption of the fluorogenic rays that we have to consider. That there is a real reaction, and not a mere optical effect, I have further proved by experiments in a pure spectrum, which it would take too long to describe.

* By this term I merely mean rays considered in their capacity of producing fluorescence: the introduction of such a term prevents circumlocution. It is convenient also to have a name for the rays emitted by a fluorescent body. If these be called, as they are a little further on, *fluorescent*, no confusion can practically result, though the term has of course a totally different signification as applied to the rays or to the body emitting them.

Hyposulphurous acid is, it is true, rather easily decomposed, but the destruction of fluorescence by hyposulphite of soda is quite independent of this circumstance. It takes place, for instance, at once on introducing a very dilute solution of hyposulphite of soda into a drop in which the fluorescence had been excited by very dilute citric or acetic acid.

After these remarks, which were necessary to prevent possible misconception, we may return to our lists. A glance at these lists shows that the classification made by the quinine reaction agrees almost exactly with the old distinction of ox-acids and hydracids. There is, however, one acid, the hyposulphurous, which in the quinine reaction ranges itself with perfect definiteness in class B, but which is not, I believe, usually ranked by chemists with the hydracids, except in so far as acids in general have been regarded from this point of view. This led me to seek whether there might not be other analogies between hyposulphurous acid and the hydracids. I have noticed the two following:—

1. It is known that a solution of chloride of mercury reddens litmus, but the blue colour is restored by an alkaline chloride, though itself neutral to colour tests. Now the very same effect is produced by hyposulphite of soda. This salt and chloride of mercury very readily decompose each other; but if very dilute solutions be used, the solution of chloride of mercury having been coloured by a little litmus, it is easy to observe that the *first* effect of the introduction of the hyposulphite, an effect which takes place immediately, prior to the formation of any precipitate, is to restore the blue colour.

2. It is known that cyanide of mercury is hardly decomposed by ox-acids, so as simply to displace the hydrocyanic acid, but readily by hydracids. Now, if a solution of hyposulphite of soda be added to one of cyanide of mercury, the smell of hydrocyanic acid is immediately perceived.

These circumstances bear out, as to hyposulphurous acid, the classification afforded by the quinine reaction. If there be a real difference of constitution between say sulphuric and hydrochloric acids, expressed in symbols by writing the former (according to the old equivalents) $\text{SO}_3 \cdot \text{HO}$, and not $\text{SO}_4 \cdot \text{H}$, and in words by calling it an ox-acid, the mere fact that the radical of hyposulphurous acid, regarded as a hydracid, contains oxygen, does not, of course, oblige us to regard it as an ox-acid. It is

that difference of constitution, whatever it may be, which must decide, and if we may trust the quinine reaction, the isolation of S_2O_3 , the analogue of chlorine, would seem to be less improbable than that of S_2O_2 , the analogue of sulphuric anhydride.

With hydrocyanic and hydrofluoric acids the reaction seemed doubtful. These acids seemed to belong to class B as regards the feeble amount of fluorescence which they developed, but not to prevent the development of strong fluorescence by acetic, sulphuric, &c., acids. Ferridecyanide of potassium had certainly no such action as chloride of sodium, or even ferrocyanide of potassium, in destroying the fluorescence; but the deep colour of the salt prevented a satisfactory decision whether the acid really belonged to class A, or resembled hydrocyanic acid in its action on quinine.

The destruction of the fluorescence of a solution of quinine in a dilute ox-acid on the introduction of a hydracid or its salt, would seem to indicate that the quinine combined by preference with the hydracid. It seemed to me that it would be interesting to restore, if possible, the fluorescence, without precipitation, by the introduction of a substance which should have a preferential affinity for the hydracid. In the case of hydrochloric acid, this may be effected by a salt such as the sulphate or nitrate of the red oxide of mercury. In trying the experiment it is convenient to use only a little hydrochloric acid, or chloride of sodium, &c., otherwise the sparingly soluble chloride of mercury and quinine is precipitated, which, however, redissolves on the addition of more of the mercuric salt. That the restoration of fluorescence is not a mere effect of the acid introduced with the mercuric salt, may be proved by varying the experiment. Let quinine be dissolved with more nitric or sulphuric acid than would otherwise have been necessary; add a little hydrochloric acid so as barely to destroy the fluorescence, and then introduce a little precipitate of oxide of mercury, stirring it up. As the oxide dissolves the fluorescence returns.

Chloride of mercury does not impair the fluorescence of a solution of quinine in an ox-acid; if anything it sometimes seems slightly to increase it. Chloride of barium, strontium, calcium, magnesium, manganese, or zinc, acts like chloride of sodium. The fluorescence destroyed by a chloride is in some measure restored by nitrate of cadmium.

When the fluorescence is destroyed by bromide or iodide of

potassium, it may be restored by oxide of mercury, just as in the case of an alkaline chloride, and under the same conditions.

The precipitate of chloride of mercury and quinine, which is liable to be produced in trying the above reactions, is strongly fluorescent, with a blue which seems to be a trifle greener than that of the solutions. The corresponding precipitate which may be obtained with bromide of potassium, doubtless a bromide of mercury and quinine, is white, and shows a pretty strong orange fluorescence, a very unusual colour for the fluorescence of a white substance. The iodide is pale yellow, and not sensibly fluorescent, at least as examined by daylight with coloured glasses.

At the conclusion of this paper, Dr. Odling made the following observations respecting the constitution of hyposulphurous acid:—

Sodium hyposulphite is usually represented by the formula $\text{Na}_2\text{S}_2\text{O}_3$, together with a molecule of water; and this molecule of water is essential, not only to the hyposulphite of sodium, but likewise to all the hyposulphites, such as the hyposulphite of barium, the double hyposulphite of silver and sodium, and the double hyposulphite of gold and sodium. If, now, instead of writing the formula of the sodium salt, as above, we put it all together in the form $\text{Na}_2\text{H}_2\text{S}_2\text{O}_4$, we have a formula which admits of being halved, and may accordingly be supposed to represent a double molecule of the sodium salt. If this be the case, the single molecule will be NaHSO_2 , corresponding to an acid H_2SO_2 .

Regarded in this manner, hyposulphurous acid forms the first term of a series whose two following terms are sulphurous acid, H_2SO_3 , and sulphuric acid, H_2SO_4 , with this difference, however, that in the two latter acids both the atoms of hydrogen are replaceable by metals, whereas in hyposulphurous acid only one hydrogen atom is thus replaceable, just as in formic acid, H_2CO_2 , which, as pointed out a few years ago by Dr. A. Dupré, may be regarded as the carbon analogue of hyposulphurous acid.

But though hyposulphurous and formic acids may be analogous, so far as their empirical composition is concerned, it by no means follows that they are analogous so far as regards their internal molecular arrangement. Formic acid is well recog-

nized by its properties to be an oxacid, that is to say an acid in which the basic hydrogen is directly combined with oxygen. With regard to hyposulphurous acid, our knowledge is far less complete; but it is quite conceivable that this acid may be a hydracid, that is to say, an acid in which the basic hydrogen is connected with oxygen (if present), not directly, but only through the medium of other elements. The difference of constitution between these two classes of acids may be illustrated by the following examples:—

Hydracids.	Oxacids.
Hydrochloric, HCl.	HOCl, hypochlorous.
Hydrocyanic, HCN.	HOCN, cyanic.
Nitrous, HNO ₂ .	HONO ₂ , nitric.

Nitrous acid cannot indeed be placed with certainty among the hydracids, but considering the great number of cases in which NO₂ is capable of taking the place of chlorine or of cyanogen, it is by no means improbable that nitrous acid may be analogous in constitution to hydrochloric and hydrocyanic acids.

The three acids of sulphur above mentioned may be formulated thus:—

$\begin{array}{c} \text{H} \\ \text{H} \end{array} \} \text{SO}_2$	$\begin{array}{c} \text{HO} \\ \text{H} \end{array} \} \text{SO}_2$	$\begin{array}{c} \text{HO} \\ \text{HO} \end{array} \} \text{SO}_2$
Hyposulphurous.	Sulphurous.	Sulphuric.

sulphuric acid being an oxacid, hyposulphurous acid a hydracid, and sulphurous acid an intermediate acid or hydroxacid. With regard to the analogy of fact between the hyposulphites and the halogen salts, the hyposulphites certainly correspond with the latter in their remarkable tendency to form double salts, the constitution of which is not satisfactorily accounted for—analogueous, for example, to the chlorides of mercury and sodium, or of mercury and ammonium. These are double salts, the constitution of which cannot be accounted for according to the commonly received notions of atomicity, unless, indeed, we follow Mr. Wanklyn in assigning to the alkali-metals, a higher atomicity than is generally accorded to them.

XII.—On the Determination of the “Total Carbon” in Cast-Iron.

By ARTHUR H. ELLIOTT.

(Read March 18th, 1869.)

SOME time ago, having occasion to determine the “total carbon” in some cast iron, I had much difficulty in finding a thoroughly convenient process. The following method, principally adapted from Ullgren (*Ann. Ch. Pharm.* cxxiv., 59), gives satisfactory results, and is easily worked.

Preparation of the Specimen.—Bore the iron with a drill; powder the borings in a porcelain mortar, picking out any large pieces and rejecting them.

Separation of the Carbon from the Iron.—Take a weighed quantity (from 2 to 2·5 grms.) of the powdered iron; treat it with 50 c.c. of a solution of sulphate of copper containing one part of the pure crystallised salt in 5 parts of water; and heat very gently for about 10 minutes. The iron will dissolve and metallic copper separate, the carbon remaining undissolved. The reason why sulphate of copper is used in preference to chloride of copper is, that it does not contain free acid, which, if present, would cause an evolution of hydrocarbons, and consequently a loss of carbon.*

Now add 20 c.c. of a solution of chloride of copper containing 1 part of the salt in 2 parts of water, and 50 c.c. of strong hydrochloric acid, and heat the mixture at a temperature near the boiling point for some time, until the separated copper has dissolved. Collect the carbon on a filter made of a piece of rather wide combustion-tube about 15 centimetres long, one end of which is drawn out to a point 4 millimetres wide, and stopped, first with broken glass (angular pieces about the size of small peas answer best), and then *loosely* with ignited asbestos. To see whether any carbon passes at first, mix the deeply-coloured solution with strong hydrochloric acid (to prevent the separation of basic chloride of copper), and then dilute with water; by this means any carbon that may have passed will be rendered visible; if the solution contains carbon, it should be boiled and passed

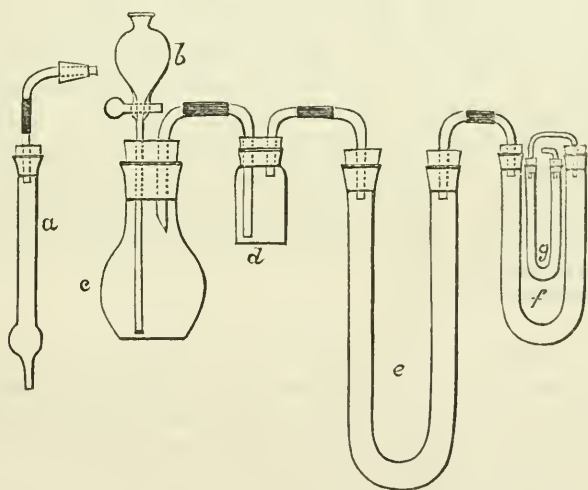
* The smell obtained when heating with sulphate of copper, is due to a small quantity of phosphoretted hydrogen.

through the filter again. Finally wash the carbon with boiling water till free from chlorides.

Conversion of the Carbon into Carbonic Acid, and Determination of the latter.—Cut the tube containing the carbon at about 2 or 3 centim. above the latter, and transfer the contents to the flask by blowing carefully into the pointed end. Wash any particles that may remain in the tube into the flask with a very fine jet of water, so as to use as little water as possible;* now add about 3 grm. of chromic acid, and attach the flask to the rest of the apparatus.

The apparatus is represented in the annexed woodcut. *a* is a tube containing soda-lime, attachable to the funnel tube *b* by a cork. *b* is provided with a glass tap. The flask *c* should hold about 200 c.c., and the bottle *d* about 60 c.c.; the latter is one-third filled with strong sulphuric acid. The U-tube *e* which is about

TOTAL CARBON IN CAST-IRON.



30 centimetres high, and about 2 centimetres in internal diameter, is filled with pumice† saturated with sulphuric acid. The sulphuric acid added to saturate the pumice should not stop the passage at the bottom of the U-tube, as this unnecessarily increases the

* If more than 15 c.c. of water is used in washing, proportionately more sulphuric acid must be added to the flask when heating.

† Previously freed from hydrochloric and hydrofluoric acids, by heating with sulphuric acid, washing and drying.

pressure to be overcome by the evolved gas. The remaining tubes are for absorbing the carbonic acid: *f* is 15 centimetres high, and 1.5 centim. in internal diameter, it is filled with good soda-lime; *g* is 9 centimetres high, and 8 millimetres in internal diameter, this is filled with pumice* saturated with sulphuric acid. Sulphuric acid is used in preference to chloride of calcium, because the latter substance does not seem competent to stop all moisture from passing it. The flexible joints must be bound with copper wire.

All being ready, add to the contents of the flask about 30 c.c. of strong sulphuric acid, through a small funnel placed in the neck of the funnel tube *b*, a small quantity at first; then shake the flask so as to mix the contents completely, and add the rest. Shake again, close the tap of the funnel-tube, and heat the flask gently till it boils. While heating the flask, the gas should not be allowed to pass the bottle *d*, faster than three bubbles in a second. When the contents of the flask boil, keep boiling for about a minute, then open the tap of the funnel-tube, remove the heat, and attach the soda-lime tube *a*. Having done this, attach an aspirator to the U-tube *g*, and draw air through the apparatus at the rate of two or three bubbles per second.

The sulphuric acid in the bottle *d* will last for three, and the soda-lime in *f* can only be trusted for two analyses; the large U-tube and the other soda-lime tube will last for about six analyses.

Test Analyses.—5 analyses of one specimen of iron gave respectively—3.40, 3.40, 3.38, 3.39, and 3.40 per cent. of carbon.

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The President remarked that in preparing the specimen of iron for analysis, a selection had been taken from the borings. Now all iron is of so complex a character, that in rejecting any part of a given sample, there is a danger of rejecting a portion of the iron having a different proportion of the metal to the carbon as compared with the rest. This, however, has nothing to do with the method of analysis adopted when the specimen has been well selected.†

* Previously freed from hydrochloric and hydrofluoric acids, by heating with sulphuric acid, washing and drying.

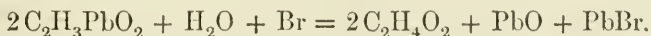
† The large pieces proposed to be rejected are those pieces which are pushed out by the point of the drill when it has nearly passed through the iron. This can be entirely obviated by not allowing the drill to bore the iron too thin.—A. H. ELLIOTT.

XIII.—*On some Decompositions of the Acids of the Acetic Series.*

By ERNEST T. CHAPMAN and MILES H. SMITH.

[Read April 1st, 1869.]

First.—Action of Bromine on Acetate of Lead.—This is not properly a decomposition of acetic acid. When bromine is added to acetate of lead in aqueous solution, a brown precipitate is at once formed. Without the aid of external heat the action stops, after the addition of a very small quantity of bromine. On warming, however, the formation of the brown precipitate proceeds until one equivalent of bromine has been added to two of acetate of lead. When this point has been reached, no more precipitate is formed, and no further action of any kind takes place, on the addition of more bromine. No gas whatever is evolved in this reaction. The brown solid is peroxide of lead, and the liquid contains bromide of lead and acetic acid. The decomposition possibly consists in the withdrawal of lead from one atom of acetate of lead by bromine, whereby peroxide of acetyl would be formed, and would at once oxidise another portion of the lead to peroxide; or the bromine may simply act in the presence of water as an oxidising agent, producing peroxide of hydrogen and hydrobromic acid, when, of course, we should get acetic acid, by the action of the hydrobromic acid on acetate of lead; the peroxide of hydrogen would oxidise the other molecule of acetate of lead, giving us peroxide of lead and acetic acid. No matter which way the decomposition really goes, it may be represented as follows:—



This equation is established by weighing the quantities of acetate and bromine employed; by weighing the peroxide of lead as sulphate of lead; and by distilling off the acetic acid, converting it into acetate of silver, and determining the silver. We think it unnecessary to subjoin the details of these operations.

Second.—Action of Bromine on Acetate of Potash.—Two equivalents of bromine, and one of acetate of potash, together with water, were sealed up in a strong digestion-tube, and heated for many hours in the water-bath. Bromine is tolerably soluble in concentrated solution of acetate of potash. After the tube had been heated for five hours, it was opened, when abundance of gas escaped—the gas proved to be carbonic acid. It was again sealed up, and again heated for about six hours. On cooling, and opening the tube, more gas escaped—still carbonic acid. The contents of the tube were still much coloured by the bromine. The action had now very nearly, if not quite, terminated. To remove the excess of bromine, a portion of the contents of the tube was treated with a dilute solution of sulphite of soda. This, of course, produced some little warmth, and an inflammable gas having an ethereal odour escaped from the liquid. Freed from carbonic acid by treatment with dilute caustic potash, this gas was found to burn with a green-edged flame, producing much hydrobromic acid. We have no doubt that it was bromide of methyl, and owed its origin to the following change—



At the same time, traces of liquid were observed, heavy and insoluble in water; probably brominated bromide. The saline product of the reaction is bromide of potassium. Acetic acid is set free, and it is impossible to push the action very far. No bromate of potassium is formed, as it must have been, had the reaction taken a different course to that described above. By the bromination of the bromide of methyl, hydrobromic acid would be set free, which would, of course, liberate acetic acid. Direct experiment has shown that a mixture of acetate of potash, hydrobromic acid, and free bromine, liberates no carbonic acid whatsoever. The reason why we cannot push the action further is, therefore, evident, viz., that the acid produced brings it to a stand-still. By distilling out the bromine, neutralising, and adding bromine afresh, we can carry the action further, until we are again stopped by the presence of acid. Simply adding alkali to the mixture, strongly coloured with bromine, has the same effect, but if we take a solution of potash, and add bromine to it so long as it is decolorised, this solution is incapable of acting on the acetate.

Bromine acts upon solution of acetate of potash with great rapidity in direct sun-light; but the action comes to a close precisely as in the former case; the products also are the same.

Third.—Action of Chlorine on Acetate of Potash in Aqueous Solution.—The action is strictly analogous to that of bromine, and like the latter, rapidly comes to a close. It can be re-started by the addition of alkali. Bi-chloride of methylene is amongst the products of this reaction; probably, under appropriate circumstances, it would furnish a convenient source of this substance. The action of chlorine is much brisker than that of bromine.

Fourth.—Action of Bromine on Valerianate of Soda in Aqueous Solution.—This reaction takes place more readily than that with the acetate of potash; and, the products of the reaction are more easily collected and examined. Aqueous solution of valerianate of soda is perfectly miscible with bromine. The mixture reacts slowly at ordinary temperatures, rather quickly in the water-bath, and with great rapidity in direct sun-light, the products being carbonic acid, and bromide of butyl more or less brominated. This reaction, like the foregoing, speedily reaches its limit, but can be re-started by the addition of potash. By fractional distillation of the liquid products, we obtained a body having about the boiling point of bibromide of butylene. We could not succeed in getting it perfectly pure, but it contained approximately the percentage of bromine required by bibromide of butylene. This substance constitutes about a third of the liquid products of the reaction. There is, apparently a very small quantity of bromide of butyl, and a very large quantity of highly brominated substance, produced at the same time.

Iodine has exceedingly little action on the alkaline salts of the fatty acids. On acetate of lead a reaction is obtained apparently analogous to the action of bromine on the same acetate. The action of iodine on valerianate of silver has yet to be investigated. At present, we only know that there is an action, and that the liquid products are of not very high boiling point. We have postponed the investigation of this reaction, until we are in possession of valerianic acid which does not consist of a mixture of isomeric acids. We have reason to believe that the action of iodine on valerianate of

silver differs with the different isomers. This reaction will, we trust, enable us to descend from a fatty acid to the alcohol immediately below it, *i.e.*, one containing one atom less carbon.

On the Action of Nitric Ethers on Acetic Acid.—A short time since Dittmar published a paper on the tension of the vapours of acetate of methyl and formiate of ethyl. In this paper he mentioned that oxalate of methyl, though hardly attacked by glacial acetic acid, is rapidly converted into acetate of methyl, if a little hydrochloric acid be added to the mixture. Similarly glacial acetic acid is almost without action on nitrate of amyl. We believe there is no action whatsoever; the addition of a few drops of sulphuric acid, however, causes a somewhat violent reaction to take place. Apparently, the same sulphuric acid can cause this reaction with an indefinite quantity of the mixed acid and nitrate.

Fifth.—*Nitrate of Amyl and Acetic Acid in presence of Sulphuric Acid.*—Nitrate of amyl was added drop by drop to a warm mixture of 20 parts of glacial acetic acid, and 1 part of concentrated sulphuric acid. No external heat is requisite after the first few moments. A regular evolution of gas is set up, and very considerable heat evolved. The evolved gases were passed through an inverted Liebig's condenser, and then collected for examination. They consisted of carbonic acid, a little nitrogen, a trace of binoxide of nitrogen, and an inflammable gas. This latter is soluble to a great extent in water, *i.e.*, water takes up four or five times its volume. It is completely and readily soluble in solution of protochloride of iron, to which it communicates a dark colour. On boiling this solution, pure nitric oxide is obtained, together with *methylic alcohol*. The methylic alcohol was recognised by converting it into iodide of methyl. An attempt was made to obtain the iodide, by passing the gases evolved directly into concentrated hydriodic acid, but without success. On sealing up some of the gas with a little hydriodic acid, and warming it slightly for an hour or so, abundance of free iodine made its appearance. The liquid products of the reaction are acetate of amyl, together with traces of acetate of methyl; the inflammable gas is nitrite of methyl. It is very difficult to give direct proof of this assertion. That it consists of methyl, together with an oxide of nitrogen, is clear; but that

it is nitrite of methyl, must rest on the fact that we know no other gaseous compound containing methyl and oxide of nitrogen, together with the facts that its very peculiar smell, taste, and method of burning are identical with those of that body. We regard these as sufficient evidence; actual proof could of course be obtained by absorbing the gas in a solution of proto-salt of iron of known strength, distilling out, measuring the nitric oxide so liberated, and then titrating the iron. This course of proceeding would be exceedingly troublesome, and appears to us superfluous. The reaction may be represented as follows, leaving out of consideration the amyl and the sulphuric acid, *i.e.*, regarding the reaction as occurring between nitric acid and acetic acid—



Taking the amyl into consideration, the reaction may be represented thus—



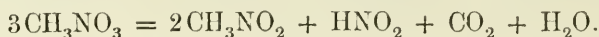
The acetate of methyl doubtless owes its origin to a secondary reaction between the nascent nitrite of methyl and the excess of glacial acetic acid.

Sixth.—Nitrate of Butyl and Glacial Acetic Acid in presence of Sulphuric Acid.—The action is precisely similar to the one above described, butyl being substituted for amyl.

Seventh.—Nitrate of Ethyl and Glacial Acetic Acid in presence of Sulphuric Acid.—Very similar to the reaction above described, differing only from it in this, that the nitrate of ethyl appears to decompose to some extent, simply by the heat of the reaction, and that we get some of the products of its decomposition along with the others. By reducing the quantity of sulphuric acid, adding the nitrate very slowly, and making the reaction proceed as slowly as it will, the result is exactly the same as when the nitrates of amyl or butyl are employed.

Eighth.—Nitrate of Methyl and Glacial Acetic Acid in presence of Sulphuric Acid.—The action here is quite different. We believe it is the methyl of the nitrate of methyl which is oxidised, and

not the acetic acid. Much red fume is produced in this reaction ; we believe it may be expressed as follows :—



Very probably a reaction analogous to that with the higher nitrates takes place at the same time. It is, however, almost impossible to prove whether the acetic acid does or does not take any part in this reaction.

Ninth.—Nitric Ethers and Valerianic Acid in presence of Sulphuric Acid.—We have made experiments on the action of the various nitrates on valerianic acid. We believe the reaction to be exactly analogous to those with acetic acid, but the excess of valerianic acid at once decomposes the resultant nitrate of butyl ; as in the case of the action of iodine on valerianate of silver, we believe that differences will be observed between the different valerianic acids, and postpone a detailed investigation until we know more of the nature, differences, and modes of separation of the valerianic acids, which are ordinarily found mixed together.

All attempts to substitute nitric acid or a metallic nitrate for nitric ethers in the above reaction proved unavailing.

Tenth.—Action of Formic Acid on Nitrate of Amylin in presence of Sulphuric Acid.—These bodies act on each other in the presence of sulphuric acid, giving rise to formiate of amyl, protoxide of nitrogen, carbonic acid, and water. Some red fume is at the same time produced.

Mr. Perkin mentioned some experiments made by Mr. Duppa on the action of chlorine on the acetates and salts of other acids, in which the chlorides of the corresponding alcohol-radicals had been obtained. Acetates thus treated yielded chloride of methyl, and succinates yielded chloride of ethylene. He himself had found that the chloride of methyl thus obtained yielded the ordinary crystalline hydrate when treated with ice-cold water, behaving in fact, just like the chloride of methyl obtained from methylic alcohol and hydrochloric acid.

The President (Dr. Williamson) inquired whether the chlo-

ride of methylene resulting from the action of chlorine upon potassic acetate, was produced in presence of water?

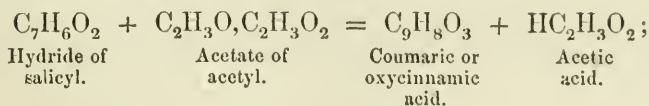
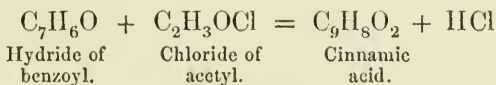
Mr. Chapman replied that it was. When chlorine is passed somewhat rapidly into a solution of acetate of potash, kept warm, and neutralized from time to time with potash, a very notable quantity of chloride of methylene is formed; but it is very volatile, and must therefore be condensed with great care, as otherwise it will be carried away with the carbonic acid.

XIV.—*Note on Coumaric Acid.*

By W. H. PERKIN, F.R.S.

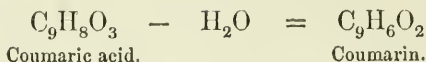
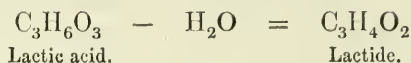
[Read April 1st, 1869.]

FITTIG, in a paper published in the *Chemical News*, on the constitution of coumarin and coumaric acid, after criticizing my theoretical conclusions, or rather speculations, assumes that coumarin is not formed from the hydride of aceto-salicyl, as I have stated, but that it results from the previous formation of coumaric acid. It will be remembered that Bertagnini sometime since stated that the hydride of benzoyl, when treated with chloride of acetyl, yields cinnamic acid, and Fittig very naturally supposed that, because I had worked with the hydride of salicyl and acetic anhydride (acetate of acetyl), I had obtained a similar reaction, and formed coumaric acid, which would then be viewed as oxycinnamic acid, thus—



and the coumaric acid, being formed in presence of acetic anhydride, and subjected to a high temperature, loses a molecule of water and gives coumarin. He therefore assumes that

coumarin is the anhydride of coumaric acid, standing to it in the same relation as lactide to lactic acid :



But the point is this,—has coumarin the properties of an anhydride at all? First of all, it is formed in the plant in presence of water; therefore one would scarcely expect it to be an anhydride. Again, you may crystallise it as many times as you like from water, and it is not changed. Moreover, you may boil it in strong potash, and you get a saline compound of coumarin; but the moment you add an acid, the coumarin separates unchanged. This is not a simple solution of coumarin in potash. It is a chemical compound of coumarin with the alkali, the nature of which I cannot quite understand. Again, on adding nitrate of silver to a solution of potash which has been perfectly saturated with coumarin, we obtain a beautiful yellow precipitate; and this compound, on analysis, gives the formula of coumarin *plus* oxide of silver; that is, $\text{C}_9\text{H}_6\text{O}_2 \cdot \text{Ag}_2\text{O}$, analogous to the silver compound obtained by Bleibtreu from nitro-coumarin. That it is a compound of coumarin is easily seen, by decomposing it with nitric acid, which removes the oxide of silver, and yields pure coumarin. Artificial coumarin, and all its homologues likewise form compounds with caustic potash, and in the case of either of the homologues, as the potash concentrates on boiling, the new compound separates on the top as an oily layer, which on cooling becomes a sticky mass. Again, if coumarin were an anhydride, it should yield an amide with ammonia; but it does not do so. Therefore, I think, that whatever the constitution of coumarin may be, it is very evident it is not an anhydride, as Fittig supposed it to be. In fact it is not an easy matter to produce coumaric acid from coumarin, a boiling supersaturated solution of caustic alkali being required.

XV.—*On the Propyl Compounds derived from the Propylic Alcohol of Fermentation.*

By ERNEST T. CHAPMAN and MILES H. SMITH.

(Read April 15th, 1869.)

IN a paper read before this Society, 18th March, 1869, we make mention of a large quantity of liquid which no amount of fractional distillation appeared capable of splitting into definite bodies. It boiled through a range of 27° , viz., from 79° to 106° . One great difficulty in its fractional distillation is, that it is nearly impossible to render it perfectly dry. It was digested with a large excess of hydrobromic acid, precisely in the manner described by us when speaking of bromide of butyl, in the paper above referred to. By this means it was converted into bromides. These bromides were carefully fractionally distilled, and split up into three fractions, the first, very small in amount, boiling below 70° , the next boiling between 70° and 71° , and the third boiling up to 92° . This latter fraction consisted for the most part of bromide of butyl, and about seven-eighths of it were obtained as pure bromide of butyl. The liquid boiling between 70° and 71° was repeatedly subjected to fractional distillation, whereby traces of liquid boiling at higher and lower boiling points were removed. The liquid now remaining weighed 284 grammes, and was, as will be proved elsewhere, bromide of propyl. It is a colourless liquid of peculiar and rather disagreeable smell, much more closely resembling bromide of ethyl than bromide of butyl. Its boiling point is between $70^{\circ}\cdot3$ and $70^{\circ}\cdot8$ under a pressure of 762 mm. bar. Its specific gravity at 16° is 1.3532.

Treated with alcoholic potash, it is readily decomposed, without evolution of the slightest trace of olefine.

With acetate of potash and glacial acetic acid, it is slowly decomposed in the water-bath, yielding acetate of propyl and bromide of potassium, not the slightest trace of gas being evolved. It is almost impossible to complete the decomposition, though more than 90 per cent. of bromide appears to be decomposed. It is not readily decomposed by acetate of silver, unless

the latter be only barely moistened with acetic acid, nor is it easier to complete the decomposition with this re-agent, than with the acetate of potash.

With dilute sodium amalgam and acetic ether, it is readily and apparently completely converted into mercury-propyl.

With cyanide of potassium and alcohol, cyanide of propyl is readily obtained.

With cyanide of mercury, decomposition is slow, and the resulting cyanide is immediately deodorised on treatment with an acid. It is in fact iso-cyanide.

Sodium has comparatively little action on the bromide, but attacks it rapidly when ether is added, and almost explosively, if sealed up and heated with the pure bromide in the water-bath.

The bromide may be agitated with concentrated sulphuric acid, without undergoing any change. If it be heated, however, decomposition takes place.

Propylic alcohol may be obtained from bromide of propyl by converting this compound into the acetate, and then decomposing the acetate with potash. As it is exceedingly difficult to complete the conversion of the bromide into the acetate, we took the impure acetate containing the trace of bromide, sealed it up with strong aqueous ammonia, and digested it in the water-bath; whereby the bromide was converted into bromide of propylamine, and the acetate, though only very partially, into the alcohol. The contents of the sealed tube were neutralised with acetic acid and distilled, the distillate saturated with carbonate of potash, and the oily layer decanted. This oily layer consists of mixed alcohol and acetate. It is treated with powdered caustic soda, which rapidly and completely converts it into the alcohol. The alcohol is dried over carbonate of potash, and then over caustic baryta.

Propylic alcohol is a colourless, tolerably mobile liquid, of a singularly intense, though not disagreeable, odour, reminding one of common alcohol, and not in the slightest degree resembling amylic alcohol. It is soluble in water in all proportions, and is by far the most difficult substance to dry with which we are acquainted. It boils at between 97° and 98° under a pressure of 770 mm. bar. Its specific gravity at 16° C. is .8120.

On oxidation, it yields propionic acid, unaccompanied by carbonic acid. Treated with strong hydriodic acid, it is converted into iodide of propyl.

Iodide of propyl is a colourless mobile liquid, resembling iodide of ethyl in smell; it boils at between 102° and 103° under a pressure of 770 mm. bar. Its specific gravity at 16° is 1.7343. It is much more easily decomposed by acetate of potash and glacial acetic acid than the bromide, and would doubtless form a far better source of the alcohol.

Acetate of propyl was not obtained free from the alcohol; it appears to be a liquid of much greater density than the generality of the acetates. Its odour somewhat resembles that of acetate of butyl, but is fresher.

Propyl compounds appear at the present moment to be in the hands of several chemists, who have already published memoirs upon them. We have not, therefore, thought it necessary to make a very detailed examination of them, and publish the above more as a confirmation of the work already done on this subject than with any other view. Fittig has recently published an account of bromide of propyl, having, singularly enough, adopted the conversion of the mixed alcohols into the bromides as a step in the process of separation, we, independently, having done precisely the same. It will be observed that we give the boiling-point of bromide of propyl a trifle lower than Fittig. Judging from his analytical numbers, his bromide must have contained a trace of some higher homologue, which would tend to account for the difference of a degree between us.

We subjoin a table showing the differences in physical properties of the normal propyl compounds, described above, and the iso-propyl compounds.

Name of Compound.	Boiling Point.		Specific Gravity.	
	Primary.	Secondary.	Primary.	Secondary.
Alcohol	97°	84°	*	$\cdot 791$ at $15^{\circ}\text{C}.$
Bromide	$70^{\circ}\cdot 5$	$60^{\circ}-63^{\circ}$	1.3532	$1\cdot 320$ at $13^{\circ}\text{C}.$
Iodide	102°	90°	1.7343	$1\cdot 70$ at $15^{\circ}\text{C}.$

The chemical differences between the primary and secondary alcohols are quite as striking as the physical ones. Iodide of

* The specific gravities of the primary compounds are all taken at $16^{\circ}\text{C}.$

normal propyl and ethylate of soda give rise to ethyl-propyl-ether and *no* propylene. The iso-iodide is almost wholly converted into propylene; the normal alcohol yields propionic acid on oxidation; the iso-alcohol, acetic and carbonic acids.

NOTE.—In our fractionation of fusel-oil we obtained two or three litres of a liquid, which consisted for the most part of ethylic alcohol, but contained traces of a higher alcohol. This liquid boiled at between 78° and 80° , and it appeared a hopeless task to separate out the higher alcohols by fractional distillation. Since the above work on the propyl-compounds was completed, we have devised a method by which this separation can be effected. The alcohol is mixed with twice its volume of hydriodic acid, of sp. gr. 1.7, and the mixture distilled. The distillate consists of an alcoholic iodide, alcohol, and water. The whole of the higher alcohols are converted into iodides, and are found in the first portion of iodide which distils over. The latter portion consists of pure iodide of ethyl. The iodides may, of course, readily be separated by fractional distillation.

APPENDIX.

Evidence on which the above account of the primary propyl compounds rests.

A. Combustion of bromide propyl.

I. Burnt with chromate of lead and copper turnings, .9214 gm. of the bromide yielded .9861 CO_2 and .4768 H_2O .

II. Digested with nitric acid and nitrate of silver, .3838 yielded .5872 of bromide of silver.

From these data the following percentages are calculated:—

		Theory.	Found.
C_3	36	29.27	29.19
H_7	7	5.69	5.75
Br.....	80	65.04	65.11
	<hr/> 123	<hr/> 100.00	<hr/> 100.05

The equivalent deduced from the determination of bromine in this analysis is 42.87, instead of 43.

B. Proof that we are dealing with normal propyl.

The alcohol oxidised with 10 per cent. chromic solution

yielded an acid which, converted into a baryta-salt, gave the following numbers:—

Salt taken 0.2985 yielded 0.2475 sulphate of baryta.

Therefore, 48.75 per cent. of barium. Propionate requires 48.41.

C. Purity of the alcohol and of the iodide were reciprocally determined by the yield of iodide from the alcohol. The operation was conducted on a small scale, and could only pretend to approximate accuracy.

8.00 of the alcohol were sealed up in a digestion tube with great excess of hydriodic acid, and the tube heated in the water-bath for a few minutes. It was cooled, and opened, its contents transferred to a small distilling vessel, water added, and the whole carefully distilled. When the iodide ceased to come over, the condenser was allowed to get hot, whereby all the small drops of iodide adhering to it were driven out into the receiver. The iodide in the receiver was shaken with a little cold water, which caused it to collect in one large drop. It was carefully removed with a pipette, transferred to a tarred flask, and weighed. It weighed 22.8 grms. The iodide was, of course, wet, though no drops of water could be seen adhering to it. Assuming it to contain 1 per cent. of water, certainly more than it did contain, we obtained 22.57 as the yield of iodide.

100 parts of propylic alcohol should yield 283.3 of iodide.

Assuming our allowance for moisture to be correct, we obtained 282.13.

Making no allowance for moisture, we obtained 285.00.

Of course as the moisture was not actually determined here, and indeed hardly could be on so small a portion, this number only shows that the alcohol was very nearly pure. We adopt 1 per cent. of moisture, simply because in various other iodides in which we have actually determined the amount of moisture, it varies between .5 and .8 per cent. 1 per cent. is therefore certainly sufficient to cover the moisture.

XVI.—*Note on Bromide of Amyl.*

By ERNEST T. CHAPMAN, and MILES H. SMITH.

(Read April 15th, 1869.)

THE properties of this substance are generally inaccurately given, or not given at all. Thus, in "Watts's Dictionary" neither boiling-point nor specific gravity is given. In the last edition of "Miller's Elements of Chemistry" both are given incorrectly.

Bromide of amyl is a colourless mobile liquid of peculiar and not unpleasant odour. It boils at 121° C. at the normal pressure; its specific gravity is 1.217 at 16° C. It rotates a ray of polarized light to the right, when prepared from a rotating sample of amylic alcohol. The bromides both of rotating and non-rotating amyl appear to have the same boiling-point; at any rate after repeated distillations the first and last portions still rotated absolutely alike. The bromide at its boiling-point is very energetically attacked by sodium.

The bromide above described is prepared by saturating amylic alcohol with hydrobromic acid gas, mixing this solution with its own volume of aqueous hydrobromic acid, and digesting the mixture in a closed vessel in the water-bath for an hour or so. It may be made without the use of pressure-vessels, by heating the mixture in a flask to which an inverted condenser is attached. The heat must, however, be very gradually applied in this case, and a certain amount of hydrobromic acid is necessarily lost. In either case, the bromide rises to the surface, and is to be decanted, washed with water, and distilled from under aqueous solution of carbonate of soda. The heavy layer found in the receiver is now to be carefully dried and fractionally distilled to remove traces of bromides of lower boiling points.

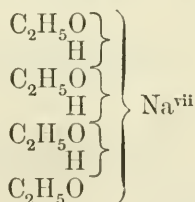
It appears to be very doubtful whether the pure bromide of amyl is obtainable by treating amylic alcohol with bromine and phosphorus, or by treating bromide of phosphorus with amylic alcohol. In the one case we are sure to obtain bromination of the alcohol; in the other, amylene or paramylene is likely to be formed. The presence of this latter compound

would naturally depress the specific gravity, and thus account for the error in that datum. In Limpricht's "*Organische Chemie*" the sp. gr. is given as 1.1658 at 0°, a result obviously considerably over 4 per cent. in error.

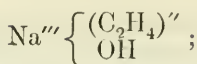
XVII.—*On the Atomicity of Sodium.*

By J. A. WANKLYN.

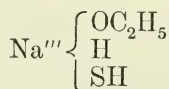
ON a former occasion I mentioned that researches, in which I had been engaged for some time, on the action of sodium on alcohol, led me to assign to the product of the re-action, a constitution different from that which is ordinarily received. I regard sodium as an eminently polyatomic element, and I consider I have evidence in support of this statement. When sodium acts upon alcohol it operates upon four molecules of that body. One molecule of alcohol is attacked in its interior, and the other three molecules of alcohol are joined on to the compound. The compound thus produced has tolerable stability; it is exceedingly light; it melts at 100° C., and will bear heating to the boiling point of water without alteration. I regard its composition as follows:—



Sodium I regard as septivalent. The formula above given represents the composition of the crystals that were supposed to be ethylate of sodium. When these crystals are heated considerably above 100° C. the alcohol goes off slowly, and if the compound is maintained for a long time at 200°, all the three molecules of alcohol go off, and the sodium is left in union with the residue. I believe that when this takes place, the sodium invades the molecule in such a manner as to form the compound—



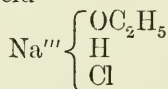
so that the sodium is in union with the representatives of three hydrogens. I have made a number of experiments on the action of this body, which I have called the *absolute ethylate of sodium*, or *hydrated oxide of ethylene-sodium*. With sulphuretted hydrogen there is, first of all, addition. If absolute ethylate of sodium be treated with an excess of sulphuretted hydrogen, it unites with just one molecule of that body, forming the compound—



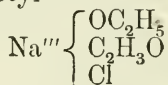
This compound has considerable stability, but breaks up very slowly at 100° into sodium, alcohol, and sulphuretted hydrogen.

The following compounds are obtained by treating the hydrated oxide of ethylene sodium with various reagents:—

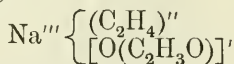
With hydrochloric acid—



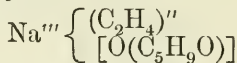
With chloride of acetyl—



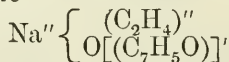
With ethylic acetate—



With ethylic valerate—



With ethylic benzoate—

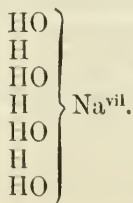


All these compounds have considerable stability, but when heated to 100° or 150° they decompose, the second, for example, splitting up into sodium chloride and ethylic acetate.

The President remarked that the question of the equivalent value of elements was one, as to which there was at present some

difference of opinion. Mr. Wanklyn's views were likely to be useful if followed up by himself and others to a definite conclusion. He thought that in many parts of our progress in science, we attend too exclusively to one particular order of phenomena, without comparing our conclusions with those derived from other parts of science. Until we obtain a compound of sodium with three monad elements, we must have some hesitation in regarding that metal as a triad. At the same time he thought it quite natural to suppose that a monad, such as sodium usually appears to be, may, in certain cases, act as a triad. But it is doubtful whether it would be desirable to assign to sodium those functions which it appears to assume in exceptional cases, rather than to say that it is a monad, and explain the exceptional cases by the special hypotheses which seem to suit them best. The combination of sodium with three equivalents of acetyl seems to favour Mr. Wanklyn's view; but when we have three times that group, acetyl (each containing two atoms of carbon, three of hydrogen, and one atom of oxygen) a union of the elements of the three radicals amongst themselves may be conceived, forming a radical which may itself be monadic. He (the President) thought that organic bodies must generally obey those principles which are clearly established among mineral compounds.

Mr. A. Vernon Harcourt could not understand why it is not more natural to suppose that the combination of these other molecules of alcohol, with what, till now, has been regarded as a molecule of sodium alcohol (ethylate of sodium), should not rather be analogous to the combination of water of crystallisation with a hydrate, or with any other salt. Take the case of sodium hydrate, NaHO , for example. This hydrate can take up an additional quantity of water. By gradually evaporating the solution, we can obtain crystals, which, if they contain three molecules of crystallisation-water, might be represented, according to Mr. Wanklyn's views, by the formula—



The hydrate thus represented would be similar in composition to the new sodium alcohol, and would furnish an argument, though a very weak one, for regarding sodium as heptatomic.

A short discussion then ensued between Dr. Debus and Mr. Wanklyn as to water of crystallisation, &c., of compounds; after which

Mr. Chapman said that unless we are prepared to abandon the atomicity theory, we must admit that when two compounds unite, they have a bond with which to hold themselves together. The fact that chloride of sodium is capable of combining with any other compound, appears to afford almost perfect proof that either chlorine or sodium—most probably both—is not a monad; otherwise chloride of sodium must be a perfectly saturated compound, incapable of combining directly with anything else.

After some further remarks by Dr. Debus, Mr. Chapman, and Mr. Newlands,

The President said that these words *atomicity* and *equivalence* had received very distinct definitions, which really ought to be adhered to. The only consistent use of the word *atomicity* was to denote an unchangeable kind of equivalence, which was believed by some chemists to exist. Some speakers had used the word in a very different sense that evening, and, he thought, in one that is usually conveyed by the word *equivalence*. Introducing such words as *bonds* he believed to be quite unnecessary, because no bonds are seriously believed to exist, and the habitual use of such a word must be productive of very considerable injury to the theoretical habits of those who employ it: moreover, no real relations of the elements are expressed by the word which may not be expressed equally well without it. Whether the atomicity theory or the equivalence theory is right, they are different. For his own part he thought that, as a rule, elements are capable, under different conditions, of assuming different replacing values; but it would be going a little beyond the fact to assume that they all possess this capability. Still, the common case is that the elements change their equivalent value, and it is, at all events, reasonable to suppose that they all do so, and by increments of two.

XVIII.—*The Chemistry of the Blast-furnace.*

By I. LOWTHIAN BELL.

THERE are many circumstances which conspire to invest the subject of iron-making with peculiar interest to the student of almost every branch of science.

To the political economist, after the means of providing food and clothing for a nation are secured, it is no exaggeration to say that iron, from its various applications, occupies a foremost place in point of importance. Without this metal, coal, the very foundation of our national greatness would, practically speaking, be beyond our reach; and not only have the great strides in facility of intercommunication of our own time been promoted by its possession, but the very idea of a railway as at present existing, or of driving a vessel against wind and tide, could never have suggested themselves had cheap iron not been at our command.

In its manufacture a knowledge of almost every division of physical laws is constantly appealed to, but it is to chemistry that the metallurgy of iron is most indebted, and hence it is to the chemical philosopher that this section of our national industry most commends itself.

The position of iron as a necessity of civilized life, the extent of its production, along with the complicated series of chemical changes which accompany the treatment of its ores, and the subsequent processes involved in the working of this metal, have attracted for it a much greater amount of attention from the chemist than has fallen to the share of any other section of the metallurgist's art.

This interest has been greatly magnified by the extraordinary influence exercised by the presence of certain substances on the qualities of the product, as well as by the extended range of character which the addition of a trifling quantity of foreign matter is capable of conferring on iron itself. We have thereby placed at our disposal this metal under three well known forms, viz., cast iron, malleable iron and steel, each being endowed with properties so peculiar as almost to merit, so far as its own

use in the arts is concerned, being regarded as a distinct metal.

On being honoured by the President and Council of this Society to deliver to its members an address on some branch of applied chemistry, I have selected the blast-furnace as a subject replete with interest, and in the hope that the opportunities I have enjoyed for many years as an iron manufacturer may justify the choice I have made.

The ground to be gone over has, it is true, been already travelled by many distinguished chemists during the last forty years, but possibly it may interest those whom I have the honour of addressing, to hear how far the experience of a practical smelter accords with the views of scientific men, whose means of observation have necessarily been more limited in their duration and character than his own.

All present have probably witnessed the various operations carried on in connection with the smelting of iron in a blast-furnace. Into the throat of a great building large barrows of rough-looking materials are shot by powerful men. At the lower portion of the edifice matters are conducted upon a scale of corresponding rudeness. At three sides a roaring blast is being poured into the furnace, while from the fourth, running almost incessantly, is a current of highly heated slag, which is dealt with in the roughest of fashions.

Generally without any protection from the weather, the "keeper" is occupied in moulding his "pigs" in coarse sand, or in maintaining his blast-pipes free from all obstruction, until the time arrives, when by mighty blows he drives in the tapping bar in order to afford an exit for the molten iron destined to fill the rude spaces prepared for its reception.

When everything seems forced into obedience by intense heat or violent exertion, there is, one might think, nothing left for milder treatment to accomplish; yet notwithstanding all appearance to the contrary, there are few chemical processes requiring for their proper operation greater nicety, or where perfect success is contained within narrower limits than the smelting of iron.

In a few words, I may remind you that the ends sought to be accomplished in the blast furnace are the deoxidation of the peroxide of iron, which is the usual form of combination in which the metal is delivered to the smelter. its carburization and

fusion; accompanying this is the expulsion of carbonic acid from the limestone, and the union of the lime it contains with the earthy matters associated with the ore and fuel to form a fusible slag.

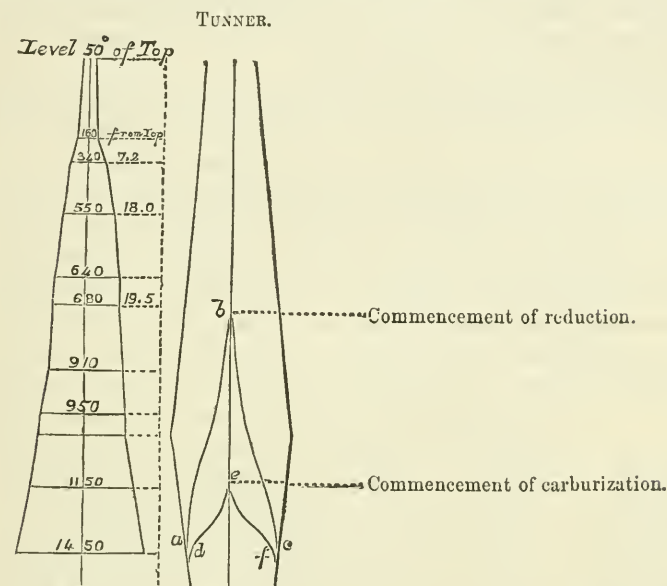
In this brief description the fuel employed is supposed to be coke or charcoal; for should raw coal be used, the hydrocarbons and other volatile constituents emitted on the application of heat may be left out as forming no necessary part of the process we are about to consider.

The circumstance of the different stages of the operation, to which allusion has just been made, being effected at different temperatures, has led some chemists to divide the interior of the blast furnace into a certain number of spaces or regions, and designate them according to the character of the action which was supposed to be carried on therein. Scheerer, among others, assigns a distinct zone, in which he imagines that each of the various steps of the process of smelting is more or less effected. The uppermost one he calls the warming zone, in which the ascending current of gases imparts a portion of its heat to the materials just entering the furnace; the second is the reducing zone, where the oxide of iron begins to part with its oxygen, and in which also the carbonic acid of the limestone is expelled; in the third, carbon is supposed to unite with the iron, which, along with the earthy constituents of the materials, is melted in the fourth or zone of fusion, by means of the intense heat given off immediately below in the fifth, or zone of combustion. It is into the last zone that the blast is admitted, the oxygen of which is almost instantaneously converted into carbonic acid, which gas, coming in contact with incandescent coke or charcoal, as the case may be, generates carbonic oxide to serve as the reducing agent in the upper portion of the furnace.

The annexed figure will convey an idea of the manner in which Scheerer conceived the interior of a furnace was divided, and the space he allotted to each division of the operation, and alongside of it is placed a diagram indicating the supposed increase of temperature.

More recently Professor Tunner, of Leoben, has by means of different alloys and various metals, attempted to determine the temperatures of two furnaces in Carinthia, and this distinguished metallurgical chemist further endeavoured to ascertain by actual exposure of ore at different depths of the furnace, the exact

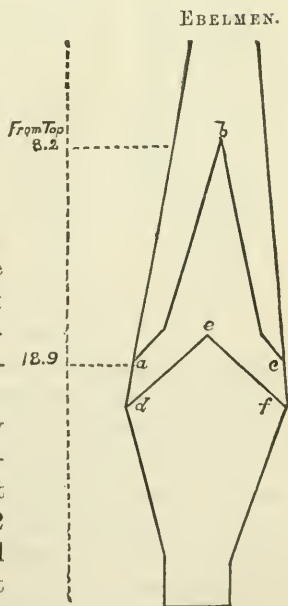
ore was introduced into the furnace, and at which the temperature was as high as 700°C . (1292°F .)



I am not acquainted with the means Scheerer employed to obtain the data upon which he constructed his diagram, but it will be observed there is a marked difference between the views of this chemist and those just described.

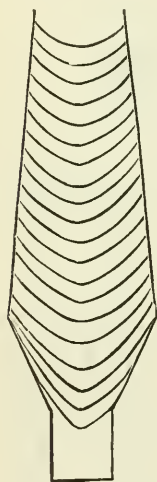
Upon Scheerer's figure I have laid down, for the sake of comparison, the curved lines *a*, *b*, *c*, and *d*, *e*, *f*, to mark the beginning of the reducing and carburizing zones, according to the principle adopted by Professor Tunner.

Ebelmen, at Clerval, in France, by means of apparatus similar to that employed by Tunner, ascertained that reduction commenced at a depth of 8.2 feet from the top, after the ore had been two hours in the furnace, and that it was completed at a depth of 18.9 feet



from the throat after an exposure of 6 hours 25 minutes, by which time incipient fusion had set in. The line *a, b, c*, represents in the adjoining sketch the rate of reduction as observed by Ebelmen, and *d, e, f*, will be something like the upper limit of his supposed zone of carburization.

My own experience leads me to question whether any such lines of demarcation as those described by the authorities just quoted can be laid down in any blast furnace, because to do this within any reasonable limits, would require that each fragment of ironstone is descending with the same speed as all those introduced at the same time, and that every piece is susceptible of being deoxidized as rapidly as the remainder. Now neither of these conditions prevails, on the contrary, the very reverse is known to take place. The friction of the materials against the sides of the furnace, particularly when they reach the slopes



immediately above the tuyeres, retards considerably the descent of those portions exposed to its influence. This is a recognized fact within the observation of every furnace manager, who knows that any change in the relative proportions of the minerals does not make its presence felt at the lower part of the furnace with all the suddenness with which it was made at the top; but the alteration in the working takes place somewhat gradually, as if the first charges of the change presented the apex of a cone something in the manner of the curved lines in the annexed ideal section.

The uniform motion of the mass downward is further liable to considerable disturbance by the smaller pieces of ironstone outrunning the larger, by slipping through openings in the contents of the furnace, a mode of progress which cannot happen with those of larger dimensions.

The correctness of this supposed interference of a uniform downward motion of the materials in a blast furnace, was confirmed experimentally by the elder Tunner, who filled one with a given quantity of charcoal before he put in any ore, and also at the same time placed in different positions in a given horizontal section pieces of marked wood. Instead of lighting the furnace when it was thus filled to the top, Tunner drew out

its contents by manual labour, by which means he ascertained that portions of the ore arrived at the bottom in little more than one-third of the time occupied by the charcoal introduced at the same period. In like manner the marked pieces of wood placed near the middle of the furnace came down much more rapidly than those which had been retarded by rubbing against the wall of the structure.

Again the size of the pieces of ironstone exercises a marked influence on the rapidity of the chemical action, which the oxide of iron has to undergo during its passage through the upper portion of the furnace: supposing therefore two pieces of ore to be travelling side by side, one containing a cubic inch of matter, and the other a cubic foot, the metal in the former will be nearly perfectly reduced almost before any action has commenced on its neighbour. In like manner the expulsion of the carbonic acid from the limestone will be greatly retarded by the size in which this mineral is employed in the process of smelting.

The same delayed action will happen, if a considerable quantity of small material is permitted to accumulate in a given portion of the interior of the furnace; indeed there is, perhaps, no circumstance which more frequently deranges the operation than this, unless special precautions are adopted to prevent its occurrence. Tipping the materials into one side of a furnace, by which the greater portion of the fuel, and the larger pieces of ore and limestone run to that opposite, never fails to act in a most prejudicial manner. I have seen furnaces have their weekly make increased by nearly one-half, and their consumption of fuel economized to an extent of 30 per cent. by simply altering the mode of charging. Upon another occasion the throat of a furnace was reduced from a diameter of $4\frac{1}{2}$ feet to one of 3 feet. The effect of this was concentrating, as it were, the smaller pieces into a column; because, as soon as the materials reached the wider part of the furnace, the larger fragments would roll to the outside. This column more or less unbroken would descend to the hearth, and from its impervious character, in an imperfectly deoxidized condition. This gives rise to a cooling action in that part of the furnace where the heat is required to be the most intense, and unreduced oxide of iron, acting as a base, enters into the composition of the slag, and thus causes a loss of metal, as well as a deterioration in the quality of the product. It is, perhaps, worthy of remark,

that a temperature represented by 2,000 units per minute, according to the French scale, is sufficient to reduce the quality of the iron one number in the scale. When it is remembered that this represents only about two pounds of coke, the assertion that the smelting of iron, in spite of its apparent roughness, is a somewhat delicate operation, will scarcely be considered as an exaggeration.

The information which is sought to be obtained respecting the temperature of the different sections of a furnace is attended necessarily with considerable difficulty. The materials which occupy the interior are difficult of penetration, and the temperature itself is so high, as to offer serious obstacles to its estimation; there are besides constant changes in the character of the chemical action which necessarily will cause corresponding changes in the temperature of any particular locality. These variations may be increased from alterations in the direction of the current of heated gases, as they meet with greater or less opposition to their progress, and the nature of the fuel itself may, by the increased power its texture may confer on it of decomposing carbonic acid, all tend to complicate the question.

Tunner and Ebelmen's mode of judging of the rate of the reduction might be accepted as an indication of what it is under the most favourable circumstances as to size, inasmuch, as in their apparatus of limited capacity they only introduced pieces of ore having very small dimensions. The very circumstance, however, of the mineral being encased within a box introduces an element of difference between the samples under experiment and those in the furnace. My own observation would indicate that the oxide of iron, when exposed to the unimpeded action of the gases of a blast furnace, is reduced at a temperature considerably below that assigned by any of the authorities already referred to, and further that the rapidity of the process is materially interfered with by any protection like that involved in the use of such a vessel as that described by Messrs. Tunner and Ebelmen.

I will now, as briefly as possible, give you the reasons founded on actual experiment, which have led me to adopt opinions in reference to this portion of the action of a blast furnace which are at variance with those of others, whose writings I have consulted, as containing the latest observation on the subject.

It may be remarked in the first instance, that the material

operated upon was the ironstone of Cleveland, but in order to ascertain to what extent previous experimenters had obtained results differing from my own, by the use of other varieties of ores, specimens of red and brown hematites and spathose ore were subjected to the same mode of treatment as that pursued with the stone smelted in our own furnaces.

In order to form some judgment of the temperature and rapidity with which the oxide of iron in the calcined oolitic ironstone of Cleveland was reduced by means of carbonic oxide, a glass tube was filled with pieces about the size of hemp-seed, and heated short of redness, probably about 300 C. (600 F.) In this state a stream of carbonic oxide was passed over it, and the resulting gas collected and examined. It contained 96 per cent. of carbonic acid, showing that a very small proportion of the original gas had escaped unchanged by the oxide of iron. A portion so treated was then examined, and found to have, in the space of 15 minutes, lost 39 per cent. of its oxygen.

After this a very large number of specimens of calcined ironstone were exposed at various times to the escaping gases of the furnaces at the Clarence Iron Works for periods from one to ninety-six hours. The furnaces vary in height from 48 to 80 feet, with a capacity of about 6,000 to 26,000 cubic feet. As might be expected, the escaping gases differ in temperature according to the dimensions of the furnace—those from the larger being cooler by their passage through a greater quantity of solid material before they reach the top where the outlet is placed. The ironstone, broken to about the size of hazel nuts, was placed about 6 or 8 feet from the furnace in the tube for conducting the gas to the boilers and hot-air stoves.

The commencement and termination of the process of reduction, it will be recollected was given as follows:—

	Began.	Ended.
By Scheerer	400 C. (752° F.)	1000 to 1200 C. = (1832 to 2192) F.
„ Tunner	680 (1256)	1400 = (2552 F.)
„ Ebelmen	Below red heat	Incipient fusion of ore.

If, then, it can be shown that the temperatures of the escaping gases at the Clarence furnaces rarely exceeded the lowest of these, and frequently were considerably below that, it follows, if these figures are correct, that little, and in most cases, no oxide of iron could have been reduced when exposed to their influence.

The specimens, previously thoroughly dried, were examined for iron before and after exposure, and the difference would enable us to estimate the loss of oxygen should any take place.

The following table will afford at a glance the results of these trials, among which there occurs only one single instance in which no change in the composition as regards oxygen appears to have been effected:—

Furnace Number	Cubic Capacity approximately.	Hours of Exposure.	Remarks.	Indications of Temp.			Loss per cent. of original O.
				Melted.	Softened.	Not affected.	
2	11,600	1	After dinner hour	Bi		Pb	4.20
6	26,500	1		Bi	Pb	Zn	5.31
7	15,400	1		Bi	Pb	Zn	4.20
4	6,000	1		Pb	Pb	Zn	5.31
2	11,600	2	Includes dinner hour; no charging.	Bi	Pb	"	4.75
7	15,400	2		Bi	Pb	"	4.75
6	26,500	2		Bi	Pb	"	6.10
4	6,000	2		Pb		"	11.83
6	26,500	3	Furnaces all quite full.	Bi		Pb	0.00
2	11,600	3		Bi	Pb	Zn	.97
7	15,400	3		Bi	Pb	Zn	4.75
4	6,000	3		Pb		"	6.10
4	"	6	Trial continuous. Record of temperature means since each preceding observation.	Zn		Stb	50.51
"	"	12		Stb			52.66
"	"	18		Zn	Stb		58.19
6	26,500	24	Trial continuous at each furnace, samples exposed in a perforated box.	Pb		Zn	3.72
4	6,000	24		Zn	Stb		35.77
6	26,500	48		Pb		Zn	5.71
4	6,000	48		Zn		Stb	48.83
6	26,500	72		Pb		Zn	27.82
4	6,000	72		Stb			54.02
6	26,500	96		Bi		Pb	27.16
4	6,000	96		Stb			57.12
2	11,600	24	Sample on tray.	Not recorded; probably melting point of Stb.			53.64
4	26,500	24					100.00

It is only right to remark that partly from a little dust being liable to be deposited on the specimens during exposure, and partly from other causes, which will be hereafter spoken of as adding to the weight the result given in the column showing the loss of oxygen is rather under than overstated.

Conceding that the gases from the largest furnace are the coolest, as really happens, and those from the smallest the hottest, the deoxidation, as might be expected, is the most

vigorous from the furnace of the least dimensions, and generally speaking, decreases with each addition to the capacity.

It will also be observed that where the fragments of ironstone were placed, not on an open tray but in a perforated box, something after the method pursued by Messrs. Tunner and Ebelmen, the amount of reduction was sensibly interfered with.

In the instance of the last sample mentioned in the list, where all the oxygen was removed, the gas given off by the addition of hydrochloric acid was found to be entirely hydrogen, with the exception of a small quantity of carbonic acid, which existed in the ore previous to exposure.

On examining the composition of the gases taken from that part of the Wrbna furnace, where, according to the former gentleman, deoxidation first manifests itself, it was noticed that they contained a very much smaller proportion of the reducing agent, viz., carbonic oxide, than those to which the samples had been exposed at the Clarence works; and as this difference might possibly affect the rate of the action on the ore, 15 litres of a mixture was prepared resembling, so far as carbonic oxide, carbonic acid, and nitrogen are concerned, the composition of the Wrbna gases, and a similar quantity corresponding, in respect to these substances, with the gases of the Clarence furnaces.*

These quantities were separately passed over Cleveland calcined ironstone in 1 hour and 45 minutes in one case, and in 1 hour and 50 minutes in the other. During the progress of the experiments twelve samples of each were collected and tried for carbonic acid. From that resembling the gases in Professor Tunner's investigations, the average volume of carbonic acid was 28·4 per cent. of the whole, and in the case of the gases of the Clarence furnaces, 35·7 of the total volume.† Both

* Composition of gases used in experiment by volume :—

	COH ₁	CO ₂	N	
Wrbna	13	16	71	= 100
Clarence.....	32	6	62	= 100

† Volume per cent. of carbonic acid. Particulars of twelve trials :—

Wrbna ..	27·4	28·4 per cent.	Clarence....	32·6	34·9 per cent.
„	28·4	28·1 „	„	34·9	33·9 „
„	27·9	27·9 „	„	36·8	36·0 „
„	28·9	28·6 „	„	37·	36·0 „
„	29·	28·8 „	„	38·	36·0 „
„	29·	28·6 „	„	37·4	36·0 „

of these results indicate almost complete conversion of carbonic oxide into carbonic acid, but of the two the Wrbna mixture is a trifle more perfect, proving thus that the want of power of deoxidation was not due to its lesser proportion of carbonic oxide.

The next point to be ascertained was whether the Cleveland ironstone was not more susceptible of the deoxidizing power of the furnace gases than ores generally are found to be. For this purpose a specimen of red ore of a very close grain was selected from Weilburg, a brown ore from Wetzler, and a Spathose one from Herdorf. They were calcined to drive off water and carbonic acid, and then exposed for $7\frac{1}{2}$ hours in the escaping gases of No. 2 furnace at the Clarence works. This furnace has a cubic capacity of 11,600 feet, and in two hours had, upon a previous occasion, expelled about 5 per cent. of the oxygen contained in the calcined Cleveland stone.

In the $7\frac{1}{2}$ hours the Weilburg red ore lost 11.99 per cent. of its oxygen and the Wetzler brown ore 16.88; the Spathose ore was also evidently acted upon, but to what extent has not yet been determined.

The larger pieces of ironstone which are here exhibited after an exposure of 24 hours to the gases of blast-furnaces, prove that although mass may retard the action, and even delay its commencement until sufficient heat has been imparted, a temperature considerably below that stated by the distinguished foreign chemists whose names have been given, is sufficient to completely deoxidize ores of iron. No doubt for this time is required, but partial reduction appears to be effected much more quickly than their observations would lead us to suppose.

Although we have hitherto been considering carbonic oxide as the sole reducing agent in the gases of the blast-furnace, there are three other substances often found associated with it, which are also capable of removing oxygen from the compound this element forms with iron. They are hydrogen, cyanogen, and ammonia. In the case of a furnace employing well burnt coke from which the hydrocarbons are completely volatilized by the coking process, the only source of hydrogen will be the hygrometric moisture driven in with the blast, for all water which may be present in the materials in use will probably be expelled before it arrives at a depth where the temperature is sufficiently

elevated to effect its decomposition. In charcoal circumstances are different, for Bunsen found in it 2 to 3 per cent. of hydrogen, which was only completely expelled on the application of a white heat.

I believe the generally received opinion is that notwithstanding the strong affinity which hydrogen has for oxygen, and the extreme readiness with which it abstracts this latter gas from its combination with iron, it plays no part as a reducing agent in the blast-furnace. Although according to Magnus its reducing power over oxide of iron commences at 360° (670° F.) it would seem, if the supposition of its inertness in the blast-furnace be correct, that the presence of so large a quantity of carbonic oxide found there must interfere with the exercise of its action on the iron ore. Almost all the analyses which I have consulted exhibit a gradual increase in hydrogen towards the mouth of the furnace, as if the gradual rise in heat which the charcoal meets in descending expelled this gas without its being altered by contact with the oxide of iron, heated although the latter was, to a point to admit of its reduction by hydrogen.

With regard to cyanogen, this substance is obviously generated by the presence of soda and potash, producing cyanides of the metallic bases of these alkalies by determining the union of carbon and nitrogen. The formation, however, of cyanogen by no means appears to be an invariable consequence of the existence of these alkalies, for I have before me a sample of a mixture of the two, which was collected near the tuyeres of one of the Clarence furnaces, and in it no cyanogen appears to be present.

Messrs. Bunsen and Playfair, in their celebrated report to the British Association, assigned an important part to the reducing agency of this compound. Dr. Percy mentions that the proportion in which cyanogen occurred in the blast-furnace at Alfreton, the scene of their experiments, was so small that it was only equal to reducing 3.75 per cent. of the make. This furnace is only 39.4 feet high, and the only place where cyanogen was detected by these chemists was 34 feet from the top, a point where, judging from that which has preceded, there ought to have been no oxide of iron requiring reduction.

The fact of the disappearance of the cyanogen almost im-

mediately after its production can be probably accounted for on other grounds than its supposed action on oxide of iron. I found that one volume of it mixed with two volumes of carbonic acid, and passed over quartz pebbles heated to redness in a green glass tube, was decomposed with deposition of carbon.

It is true, nevertheless, that the mixture of these two gases in the proportions given, was found capable of removing oxygen from oxide of iron: for in 15 minutes calcined Cleveland stone lost 3·42 per cent. of its oxygen at a temperature short of redness and when the heat was raised until the glass softened 25·14 per cent. of the original oxygen was expelled.

The only instance in which ammonia ever came under my notice in a blast-furnace was in the form of chloride which dropped associated with other salts and water from the gas tube, upon the occasion of using raw instead of calcined iron-stone, by which the temperature of the escaping gases was reduced to about 40° C. (104 F.)*

At a temperature short of redness ammoniacal gas was ascertained to deprive Cleveland calcined ironstone of 2·85 per cent. of its original oxygen, and at a low red heat 17·71 was expelled. In each case the operation was continued for twelve minutes, free ammonia escaping from the open end of the tube.

Whether this alkali ever exists in a condition to enable it to act as a reducing medium in a blast-furnace I am unable to say; one thing, however, may be accepted as certain, viz., that the quantity is never such as to render its action of any importance in the operation of iron smelting, nor shall we be far wrong in assuming that for all practical purposes carbonic oxide is the sole reducing agent, to which must be referred the duty of deoxidizing the ores of iron in the furnace.

During the passage of the reduced iron through the furnace, and under the influence of the high temperature to which it is exposed on its way to the hearth, the metal is apt to carry down some of those substances with which it was originally associated in its ore, or which it meets with in the flux or fuel employed. To such an extent may this occur that Fresenius

* Composition of the substance was as follows:—

Insoluble.	Chloride ammonium.	Chlor.de iron.	Chloride Zinc.	Water.
1·0	52·9	14·7	6·6	24·8 = 100

quotes a case in which he detected and estimated the quantity of not less than twenty substances other than iron in a specimen he analyzed. In some cases as much as 22 per cent. of manganese has been found in pig iron and above 5 per cent. of silicon, the presence of the former due to the ore employed being rich in that metal, and the latter derived probably from the temperature of the furnace being high enough to decompose the silica invariably present in the materials under treatment in a blast-furnace. That neither of these elements, nor all the others mentioned by Fresenius, with one exception, are essential constituents of pig iron, is proved by the circumstance that although no cases, perhaps, are known where none occur, every one or other is occasionally absent. The one exception is carbon, which may, therefore, be looked upon as a necessary ingredient of all pig iron.

The circumstances which determine the union of this indispensable element with the metal, are of high interest to the smelter, because upon the condition in which the carbon is associated with the iron depends, it is considered, the different qualities of the article he is manufacturing.

The portion of the furnace in which the combination takes place, the temperature necessary for effecting it, and the exact source of immediate supply, have engaged the attention of all chemists who have studied the subject.

Scheerer assigns to it something like the position described by the line *d. e. f.* in his section, where the operation, he states, is effected after all traces of un-reduced oxide have disappeared, and where the temperature ranges from 1,000° to 1,600° C. (1,832° to 2,912° F.)

Tunner, by means of his perforated box, containing fragments of calcined ore, determined that carburization did not take place until a depth of 29·8 ft. from the top of the furnace was reached, where the temperature ranged about 1,150° C. (2,102° F). This patient investigator, indeed, deduces from the known heat at which carbon unites with iron, in the process of cementation, the temperature of this portion of the furnace, which, he states, accords with what it ought to be, from a direct observation made 4·33 feet higher up. He further lays down the limits of the zone, marked *d. e. f.* on his section, in which the union of the carbon with iron is accomplished.

Upon the sketch intended to show Ebelmen's idea of the

zones of reduction and carburization, the latter is somewhat higher up, but according to his views no signs of it were apparent until the wrought iron apparatus was softened by the heat, and the ore itself manifested symptoms of incipient fusion.

The conditions then deemed essential by these three gentlemen were reduction, almost, if not perfectly complete, and a temperature of something like $1,000^{\circ}$ to $1,200^{\circ}$ C. ($1,832^{\circ}$ to $2,192^{\circ}$ F.) Let us now enquire whether it is not highly probable that the exclusion of the full force of the chemical energy, which the gases of the furnace were capable of exercising, by confining the ore in a box, has not interfered with the action of carburizing in the same way as happened, in all probability, with that of de-oxidizing.

In order to ascertain the extent of the change in content of iron, the samples were, after exposure, dissolved in hydrochloric acid, a mode of procedure which afforded, of course, an insoluble residuum.

When a sample of calcined ironstone was exposed for the space of two hours in the waste gases of any of the furnaces, large or small, this residuum was of a colour inclining to grey—not calling for any special notice. The same may be said when the exposure was carried on for three hours in all the furnaces, except those of the least dimensions, from which, as we have already seen, the gases issue the hottest—zinc in them frequently melting and occasionally antimony. In a furnace of this type, such as No. 4 at the Clarence works, the insoluble residuum under consideration, from a specimen after three hours' contact with the hot gases, was blackish, and this colour went on increasing in intensity as the exposure was prolonged, until it became perfectly black. On the other hand, No. 6 furnace, having above four and a half times the capacity of No. 4, or 26,500 cubic feet instead of 6,000, never gave off its gases, during a period of observation extending over 96 hours, hot enough to melt zinc; for during 72 hours of this time lead melted, and for the last 24 hours bismuth only was fused. Ironstone, exposed during these 96 hours, only afforded a greyish insoluble residuum on being treated with hydrochloric acid.

These observations have led me to conclude that an exposure of three hours to a temperature a little above the melting point of lead, and below that of zinc, sufficed to give the black

colour, whereas at about the temperature at which lead fuses no period up to 96 hours sufficed to produce it. Probably, if we give 337°C . (630°F .), as being below the heat necessary to give the blackness, and 361°C . (700°F .) equal to afford it, we shall not be wide of the truth.

On examining into the cause of this blackening, it was found to consist of carbon, inasmuch as it totally disappeared on the residuum being heated in contact with air, and on passing a current of pure oxygen over it vivid combustion was produced and carbonic acid generated, which was recognized in the usual way. This carbon, moreover, exists in such a minute state of division as to induce me to believe that it is really combined with the iron, or is deposited by chemical action in such a form as to present great facilities for subsequent combination. It therefore seems probable that instead of the lowest and hottest portion of the furnace being the zone of carburization, this change occurs high up, where the temperature is comparatively low. Neither does it appear that anything approaching to complete deoxidation is required; for in one case where only 6.10 per cent. of the oxygen of the ore was driven off, the residuum was blackish, and with anything like 50 per cent. of loss of oxygen the colour is intensely black. On the other hand, oxygen may be removed to the extent, at all events, of 28 per cent., and no strongly marked signs of carbon appear in the residuum if the heat during exposure has not reached the necessary point of elevation.

The amount of carbon associated with the iron was determined in those cases where the exposure of the ore had been effected in a box with perforated sides and open at the top. The residuum from ore, after

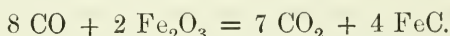
48 hours' exposure, lost 48.83 per cent. of its oxygen, and contained of the weight of iron	2.42 C. per cent.
72 hours' exposure, lost 54.02 per cent. of its oxygen, and contained of the weight of iron	3.09 C. „

while, in another instance, where the ore was placed on an open tray, all the oxygen was gone, and carbon, to the extent of 3.26 per cent. of the weight of iron was found in the residuum.*

* Time did not permit the necessary analysis being made, so as to obtain with exactness the whole of the carbon. To estimate the iron, a solution in hydrochloric

It may be observed that the residuum from all the samples of foreign ores, exposed for seven and a half hours in the gases from a furnace of medium size, showed unmistakeable signs of carbon having been deposited.

Admitting the correctness of the opinion just laid down, the following formula would account for the action, when the deoxidation and carburization is complete :—



I am, however, by no means satisfied that this equation conveys a true explanation of the action, for within the last few days I was desirous of ascertaining how far the introduction of the Cleveland ironstone in its raw state, *i.e.*, as carbonate of iron, would retard the deoxidation. The extent of this is immaterial but what is of importance is that a very considerable increase in the quantity of this deposited carbon took place in each sample exposed.

Here are five specimens of each, *viz.*, the insoluble, from the ironstone, raw and calcined, before they were placed in the escaping gases of No. 4 furnace, the others being the insoluble and blackened residuum after the two varieties, exposed at the same time, had been in for 6, 12, 18, and 24 hours:

In the case of the raw ironstone, the colour was so much blacker than when the calcined ore was used, that the quantity of carbon in each was carefully determined. With the calcined ore it amounts to 1.68 per cent. of the iron, while in the raw stone it is 4.63 per cent. of the iron, after each had been exposed 24 hours in the escaping gases.*

acid was made, during which probably a portion of the carbon was lost, and I was obliged to content myself with examining the insoluble left after treating the samples with this acid.

* *a.* Insoluble from 100 grains of calcined ironstone, in which organic matter must have been destroyed, was dried at 193 C. (380 F.) :—

Heated to redness in contact with air lost..... 0.15 gr.

b. Insoluble from 100 grains of calcined ironstone, same as above, previously exposed in waste gases of No. 4 Clarence furnace, for twenty-four hours :—

Dried at 193 C. (380 F.), and then heated to redness, lost..... .88 gr.

Deduct for loss assumed as independent of carbon..... .15 „

Leaving for carbon73 gr.

Specimens contained 43.5 per cent. of iron. Carbon therefore is equal to 1.68 per cent.

c. Insoluble from raw ironstone, exposed as such, in gases from No. 4 Clarence

It was then deemed desirable to ascertain to what extent carbon might be caused by any organic matter existing naturally in the ore and retained in the ironstone, while the latter was imperfectly calcined, and, consequently, before the carbon so formed was entirely burnt off.

When the insoluble residuum from this source was thrown into melted nitrate of potash, the faintest trace of carbon made itself apparent, whereas with that obtained in either of the two instances previously quoted, deflagration of some violence was produced.

In the minds of all practical smelters, there is no doubt entertained, that the hotter a furnace is working, the richer is the iron in graphitic carbon, or "kish," as they term it. This, together with the circumstance, that when the temperature is very high, flakes of this substance escape in considerable quantities when an opening is made above the dam of the furnace, probably has favoured the belief, that the region of fusion was the chief seat in which the union of carbon with the iron was accomplished.

It is, perhaps, a little premature to speculate upon the nature of the origin of carbon in pig iron by aid of facts, many of which have only been ascertained since this paper was begun, and some investigated so lately as yesterday. It may, however, be observed, that although this substance exists in pig iron in two distinct forms, viz., as combined, and as uncombined or graphitic, there is nothing antagonistic in the idea of carbon uniting with iron in that portion of a furnace, where no such difference of temperature is ever found likely to produce at one time white iron, in which the carbon is chiefly in the combined form, and at other time grey iron rich in uncombined carbon. It is, I imagine, quite consistent with all observation to suppose that the ore during or after the process of reduction may absorb all the carbon it requires, but the form this element

furnace, for twenty-four hours. Insoluble from 100 grains of the ironstone weighed after exposure:—

Dried at 193 C. (380 F.) and then heated to redness, lost.....	1.90 gr.
Deduct for loss assumed as independent of carbon15 „
Leaving for carbon	1.75

Sample contained 37.8 per cent. of iron, hence iron is associated with 4.63 per cent.

may assume in the pig iron produced, will depend on the temperature when fusion takes place. This explanation is corroborated by the well known fact, that white iron may be run from the blast furnace, and be changed to grey by slow cooling, and the richest No. 1 iron may be reduced to No. 3, or even rendered white by chilling it suddenly against a surface of cold metal, proving thus, that it is the latest condition of things previous to solidification which determines the character of the carbon, rather than the mode in which it has found its way into the metal.

As to the flakes of "kish" flying about a furnace making rich iron, it is possible they may be produced by the decomposition of the oxides of carbon under the influence of the high temperature and chemical action, or even by the decomposition of cyanogen, for I ascertained that this compound not only deposited carbon when heated along with carbonic acid, but that it also at a temperature of redness conferred carbon upon iron, of which it had effected the reduction.

A consideration of the other occasional constituents of pig iron would carry us far beyond the limits of such a discourse as the present; we will, therefore, pass on to review, in as condensed a manner as possible, the behaviour of lime in the blast-furnace.

One duty, but not the only one, performed by this earth, generally added in the form of its carbonate, is to act as a flux by melting and separating the solid impurities of the ore under treatment. The labours of Berthier informed us how the fusibility of any two earthy substances was promoted by the addition of a third, and what an extended range of proportions could then be used without seriously interfering with readiness of fusion. This chemist further showed how the presence of a fourth, or more substances even in very small quantities augmented fusibility. Were it not for these laws, the smelting of many of our ores would be a matter of great difficulty, if not of impossibility, owing to the endless variety of the proportions in which silica, alumina, lime, and magnesia are found associated with the metal.

Dealing with these earths alone, silica occurs in every proportion from 30 to 70 per cent. of the whole, alumina from 20 to 30 per cent., lime from 4 to 27 per cent., and magnesia

from 3 to 19 per cent., and this list merely comprehends some of the ordinary ironstones of this country.*

It is usually considered that the use of an excess of lime promotes the separation of sulphur, and it may be of phosphorus, from the iron produced, for it is frequently added when the earths naturally existing in the ironstone are in such proportions as to constitute a perfectly fusible slag. This is the case with the ore of Cleveland, as was proved by actual experiment in the laboratory, after which, one of the Clarence furnaces had lime gradually removed from the charges until it was entirely withdrawn. So far as the mere office of smelting was concerned, the operation was perfect, *i.e.*, all the iron existing in the ironstone was obtained, and a perfect slag was produced. There was some little practical difficulty connected with working the furnace, but the inconvenience which was anticipated occurred,—the iron, No. 3, contained much more sulphur, than when using lime, *viz.*, 0·33 per cent., and its quality in point of strength suffered considerable deterioration.†

It will be impossible for us upon the present occasion to dwell at any length upon the distinctive characters which mark blast-

* Proportions in which silica, alumina, lime, and magnesia exist in certain ironstones, calculated from analyses contained in geological survey of Great Britain.

100 parts consist of	Silica.	Alumina.	Lime.	Magnesia.
Darlaston	69	24	4	3
Dudley	61	29	5	5
Low Moor	60	24	9	7
Corngreaves	59	28	8	5
Rough Hay	58	20	11	11
Butterley	55	24	10	11
Dudley	53	28	13	6
Dowlais	52	23	12	13
Blaenavon	50	21	12	17
Stanton	50	20	12	13
Blaenavon	49	25	8	18
Staveley	49	25	7	19
Parkgate	44	24	13	19
Dowlais	39	27	15	19
Cleveland	31	29	27	13

† Sulphur in Clarence iron :—

No. 1 iron	·04 per cent.	No. 3	·10 per cent.
Do.	·25 „	Do.	·17 „
Do.	trace	Do.	·04 „

Vide Paper by I. L. Bell, on Cleveland Iron Manufacture, read before British Association at Newcastle, 1863.

furnace slags, which have compositions embracing so extensive a range of variations in their constituent parts. This interesting series of compounds occasionally, when silica is in sufficient quantity, possesses the properties of true glass gradually changing into substances of a perfectly stony nature, in which no trace of vitrification is usually perceptible. This is particularly the case when alunina is in such quantity, as probably to divide with silica the functions of an acid.

Mention has already been made of the difficulty which accompanies drawing any general conclusions respecting the progress of the operation of smelting from an examination and analysis of the solid contents of a blast-furnace.

Probably the most elaborate investigations into the nature of the gases taken from various depths of a blast-furnace are contained in the communication by Messrs. Bunsen and Playfair to the British Association in 1845. Judging from the drawing which accompanies the paper, the furnace at Alfreton was charged in the defective way already spoken of, viz., at one side only of the throat. It may therefore be questioned whether the current of gaseous matter would have anything like a uniform composition over any horizontal section corresponding with the point where the samples were taken.

Dr. Percy, in his review of the various analyses made by different chemists, despairs of being able to elicit any general expressions by which the chemical action of each portion of the blast-furnace can be explained, and it is to be apprehended this is a state of ignorance in which we must be content to remain.

Imagine a furnace in which pure oxide of iron is being smelted by pure carbon; now so long as the oxide was reduced in the upper and cooler portions, the extent of carbonic acid would be a correct indication of the nature of the process carried on; but wherever deoxidation is delayed, as no doubt may happen, until that depth is reached, when the high temperature would decompose this acid, then the gases afford no indication of the change effected on the solid contents of the furnace.

When we come to consider the properties of carbonate of lime when exposed to heat in an atmosphere of carbonic acid, the problem of drawing from the presence of this gas any general inference of the chemical alteration going on in a furnace becomes very intricate, if, indeed, not impossible.

This salt of lime, as is well known, parts with half its carbonic acid at a moderate red heat, a much higher temperature being required before the whole is expelled. In the solution of the question just mentioned, we have to determine not only whether all the iron is deoxidized, but also whether the temperature is such as will drive off carbonic acid from the limestone, and then whether the heat is sufficiently high to decompose the carbonic acid from either source. In the case of the ore it is quite possible that all the carbonic acid resulting from its decomposition may be formed when this change would be impossible; but in that of the limestone, it is pretty clear the last half, more or less, will not be set free until, meeting with hot carbon, it is instantly resolved into carbonic oxide.

It is by no means an uncommon thing for iron smelters to use caustic lime in their operations; this, however, does not simplify the inquiry, but rather the reverse. Up to a temperature of redness such as to soften green glass, I ascertained that lime absorbed carbonic acid in proportion to the temperature to which it was exposed, *i.e.*, the higher the heat, the more rapid was the union—this absorption went on until 19 per cent. of the weight of the lime was taken up, after which a stream of the gas, continued for nine hours, produced no further change. On the other hand, carbonate of lime and caustic lime were subjected to a current of carbonic acid in a porcelain tube, and heated until the latter began to soften. In this case there was no absorption of carbonic acid, on the contrary all the acid was driven off from the carbonate.

So far as moderate temperatures are concerned, it was ascertained that caustic lime rapidly absorbs carbonic acid from the escaping gases,* so that in addition to not knowing the rate at

* Caustic lime exposed for one hour in escaping gases from No. 4 Clarence furnace:—

Lead melted zinc not changed, absorbed of its weight				
of CO ₂				1.28 per cent.
No. 7 furnace	Bismuth melted, lead, not changed			1.00 "
" 2 furnace	ditto	ditto96 "
" 6 furnace	ditto	ditto92 "

After two hours' exposure, temperatures as above:—

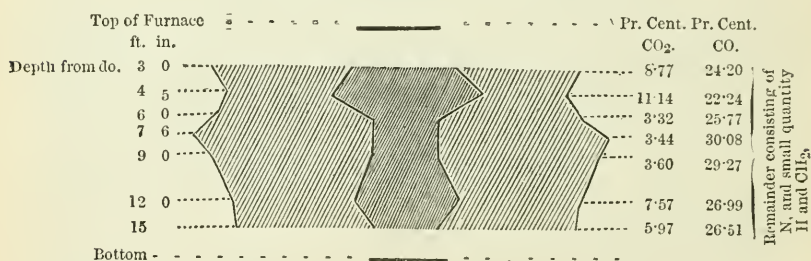
Lime absorbed of its weight in gases of No. 4 furnace..				1.72 per cent. CO ₂ .
	"	"	2 "	.72 "
	"	"	7 "	.62 "
	"	"	6 "	.52 "

which this gas was at any particular point generated by the whole mass of ore, it would be impossible to discover how much of it, so formed, was taken up by the lime, only to be again expelled in the lower and hotter portions of the furnace.

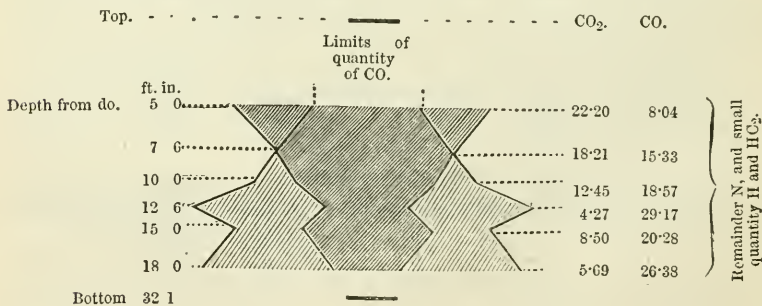
It is almost needless to say that when lime or its carbonate exists in the ores naturally, the same consequences will happen more or less as those described in the case of the earth used separately and constituting the flux.

To afford a clearer idea than figures can do of the want of uniformity in composition of the gases from different depths of furnaces, as determined by analysis, I have constructed a few diagrams drawn to a scale in which carbonic acid is shown by the darker shaded part, and carbonic oxide by the lighter. In the four diagrams the scale is according to volumetric analysis, and the authorities quoted.

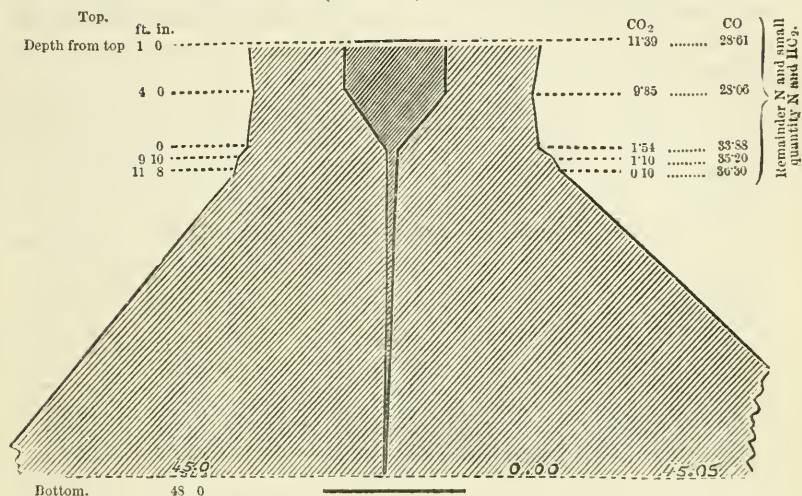
Locality, Veckerhagen. Authority, Bunsen. Temperature blast, 278° C. (532 F.) Fuel, Charcoal.



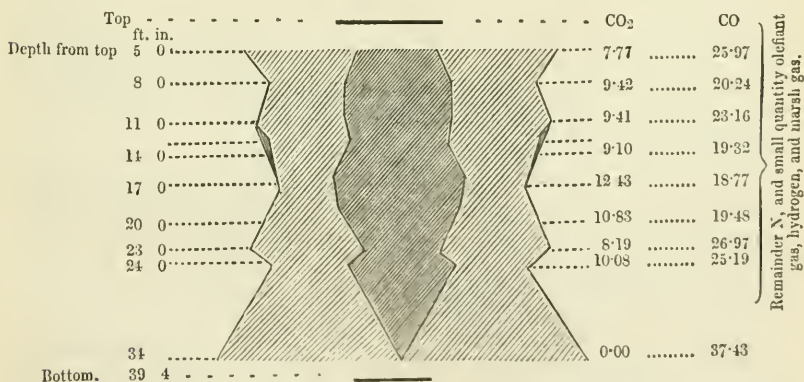
Locality, Baerum. Authority, Scheerer and Langberg. Temperature blast, 200° C. (392 F.) Fuel, Charcoal.



Locality, Séraing. Authority, Ebelmen. Temperature blast, 100° C. (212° F.) Fuel, Coke.



Locality, Alfreton. Authority, Bunsen and Playfair. Temperature blast, 330° C. (625° F.) Fuel, raw Coal.



The difficulty which attends obtaining an average sample of the gases below the level of the top of the furnace, does not present itself when the object is to procure specimens of the gases after they have left the furnace.

The following portions of gas from No. 4 Clarence furnace,

48 feet high, were carefully taken and analyzed, many in my presence, by Mr. W. Moody, the chief assistant in the Washington laboratory. The results, when the trials were repeated, are given, so that some opinion may be formed of the attention bestowed on the experiments.

Volumes of in 100 Volumes.*	CO ₂ .		CO.		N by Difference.	
	1st Trial.	2nd Trial.	1st Trial.	2nd Trial.	1st Trial.	2nd Trial.
Hour sample taken.						
1 p.m.	6·25		26·80		67·45	
1.55	6·24	6·70	34·70		59·06	
2.15	6·94	6·73	34·40	35·40	53·66	57·87
3.0	5·30	5·75	35·80	35·64	58·90	53·61
3.15	4·75	5·12	31·00	30·25	64·25	64·63
3.55	5·91		31·12		62·97	
4.20	5·82	6·00	29·72	28·90	64·46	65·10

A very brief examination of the figures contained in the above table proves how liable to variation is the nature of the changes going on in a blast-furnace, even when to all appearance the materials employed are precisely the same.

If the gases of a blast-furnace have to furnish us with any data from which we may endeavour to draw just conclusions of the nature of the chemical action going on in its interior, it appears to me that little reliance can be placed on any analyses, excepting of those of the gases as they escape.

If, as I think most probable, little, if indeed any, carbonic acid leaves the lime until it reaches a portion of the furnace when the heat is such as to resolve the liberated acid into car-

* The following figures show the above volumetric constituents converted into weights :—

	CO ₂ .		CO.		N by Difference	
Hour.	1st Trial.	2nd Trial.	1st Trial.	2nd Trial.	1st Trial.	2nd Trial.
1 p.m.	9·60	Nil	25·86	Nil	64·54	Nil
1.55	9·55	Lost	33·90	Lost	56·55	Lost
2.15	10·78	10·26	34·10	34·51	55·12	55·23
3.0	8·13	8·83	35·10	34·93	56·77	56·24
3.15	7·86	7·33	29·78	30·59	62·36	62·08
3.55	9·06	Lost	30·50	Lost	60·44	Lost
4.20	8·98	9·22	28·68	28·30	62·84	62·48

bonic oxide, it is clear that all the carbonic acid found in the gases must be due to the deoxidation of the ore, which, according to the views laid down in this paper, is effected at a lower temperature than was supposed by Tunner, and at one where carbonic acid is not decomposed by incandescent carbon. The ironstone may be in such large masses, like those on the table, that the whole of the oxygen may not be expelled until a considerable depth in the furnace is reached, and then, of course, the carbonic acid generated by the process of reduction may experience the same fate as that liberated from the carbonate of lime.

It is not a difficult matter to calculate what the composition of furnace gases ought to be, supposing a certain quantity of coke and limestone to be consumed to the ton of iron, and the sole source of carbonic acid to be the ore by its deoxidation.

Assume the coke used to be 23·20 cwts., and the limestone 11·60 cwts. per ton of pig iron, containing 19 cwts. of pure iron.

The coke may be taken as consisting of—

Pure carbon	21·80
Ash	1·40
	<hr/>
	23·20

And the limestone will consist of—

Lime	6·50
Carbon 1·39	
Oxygen 3·71 to form carbonic acid	5·10
	<hr/>
	11·60

The ironstone will consist of iron 19 cwts.

Oxygen	8·14	„
Earths.....	22·86	„
	<hr/>	50·00

The total carbon then to be dealt with is—

In the coke	21·80	
In the limestone	1·39	
	—	23·19 cwts.

From which must be deducted the carbon to combine with the iron ..

·74 „

Leaving to go off as carbonic acid and as carbonic oxide

22·45 „

The total quantity of oxygen we have in the minerals applicable to oxidizing carbon is in the—

Ore.....	8·14	
Limestone.....	3·71	
	<hr/>	11·85
To which may be added from the decomposition of water contained in the blast		·85
	<hr/>	
Cwts.....		12·70
		Cwts.
To convert 22·45 cwts. carbon to the state of carbonic oxide will require of oxygen		29·93
But as applicable to this we have in the limestone 3·71, and in the blast ·85		4·56
	<hr/>	
Leaving to be derived from the atmosphere		25·37
	<hr/>	
25·37 atmospheric oxygen is equal to nitrogen		84·93
8·14 oxygen in the ore will give, of carbonic acid generated by its action on carbonic oxide		22·38
22·38 carbonic acid contains 6·10 of carbon, leaving 16·35 (22·45 — 6·10) carbon to give of carbonic oxide		38·15
	<hr/>	
Total weight of gases per ton of iron....		145·46

Supposing then the carbonic acid from the limestone to be decomposed, and that generated by the reduction of the ore to escape as such, the proportions in which nitrogen, carbonic acid, and carbonic oxide should be found in the escaping gases, would be—

Nitrogen	58·38
Carbonic acid	15·39
Carbonic oxide.....	26·23
	<hr/>
	100·00

The analyses of the gases from a blast-furnace, making forge iron with precisely the quantity of materials named in the above calculation, gave the following results by weight :—

Taken at	CO ₂ .		CO.		N by Difference.	
	1st Trial.	2nd Trial.	1st Trial.	2nd Trial.	1st Trial.	2nd Trial.
Hour.						
1 p.m.	18·28	18·20	27·19	27·19	54·53	54·61
2.10	14·60	15·10	30·09	28·60	55·31	56·30
2.40	15·05	15·58	18·61	19·50	66·34	64·92
3.30	18·50	Lost	25·80	Lost	55·70	Lost
3.45	15·85		25·50		58·65	
4.0	16·12	16·41	23·00	24·88	60·88	58·71
4.10	19·71	19·71	23·60	23·60	56·69	56·69
4.50	19·25	19·14	27·08	27·10	53·67	53·76
Average . .	17·17		25·11		57·72	

These figures show a close approximation to the theoretical calculation, there being rather more carbonic acid, as shown by the analyses, than the previous estimate would indicate, from which it may be inferred that not only the whole of the iron-stone was reduced in the upper and cooler part of the furnace, but also that a portion of the carbonic acid which was contained in the limestone was also expelled before the flux reached a part of the furnace where the heat was intense enough to decompose it.*

On watching the slag from a furnace in the Cleveland district as it falls from a spout into the vessel for receiving it, a white fume is perceived. A portion of this may be sulphurous acid combining with hygrometric water, but by far the greater quantity consists of the earths themselves, in the state of vapour, at least such I conceive to be the case. This vaporized lime, alumina, magnesia, and silica, ascend through the contents of the furnace, and are no doubt to a considerable extent condensed

* This is consistent with observation, for in an experiment mentioned in a discussion before the Institution of Mechanical Engineers, 28th January last, I showed that coke was incapable of decomposing carbonic acid at a temperature which completely melted German green glass. Upon the same occasion I gave it as my impression, that one of the advantages in using high furnaces was that they did not permit the gases to escape at a temperature at which they were still capable of deoxidizing the ores. This latter circumstance was also alluded to by the President, Dr. Williamson, in the discussion which followed the reading of this paper. The analyses just quoted were of gases taken from a furnace 80 feet high, and containing about 11,500 cubic feet, so that as far as chemical action is concerned, its dimensions appear to be sufficient.

as a sublimate on the way, but eventually a certain quantity escapes from the top, constituting the mass of fume visible in most smelting districts, but particularly conspicuous on the banks of the Tees. At one time I supposed this volatilizing sufficient to account for a difficulty in reconciling the composition of our slags with the earthy materials which really entered the furnace. This discrepancy I have since ascertained is due to the great variations in the composition of our ironstone itself. As might be expected, the higher the furnace in which the smelting is being carried on the greater is the interception of these vapourized earths and the other substances associated with them, but the actual quantity varies in the same furnace at different times.

From a furnace 48 feet high, the quantity amounted upon one occasion to 59·09 lbs. per ton of iron made, and at another to 77·31 lbs., while in an 80 feet furnace the weight for the same quantity of metal was 27·24 and 19·54 lbs. respectively upon the two days when the experiment was made.*

To this short account of the gases I would only add that instead of escaping into the atmosphere and burning at the tops of the furnaces, as formerly happened, and still happens generally in Staffordshire, and uniformly so in Scotland, the carbonic oxide they contain is burnt for raising steam for the blast engines, and for heating the air, by which something like

* The estimated weight of slag per ton of iron is about 30 cwts.

The following shows the composition of this condensed fume, taken out of the gas-pipes:—

Silica and sand	44·82
Alumina.....	16·00
Lime.....	12·15
Magnesia.....	·57
Peroxide of iron	8·20
Oxide of zinc.....	4·60
Sulphuric acid	8·80
Potash.....	·40
Soda.....	6·85
Chlorine	1·56
Water	5·60
	— 99·55

Report, I. L. Bell to British Association, 1863.

A second sample was collected by drawing through water for some hours the gases

a saving of 600,000 tons of coal per annum is effected in those works smelting the ironstone of North Yorkshire.

Having now traced the progress of the solid materials down through the furnace, and considered the action of the gaseous current flowing upwards among them, let us devote a few minutes to an examination of the blast by means of which we obtain heat from the fuel to fuse the iron and slag, and generate carbonic oxide to effect the reduction and carburization of the metal, which is the object of the process.

The effect of cold on our atmosphere being to deprive it of a considerable portion of its moisture, and to contract its bulk, a cubic foot of air in winter contains of course less watery vapour and more oxygen than is embraced within the same space in summer.

It is obvious that there is no necessary connection between a rise in temperature and the presence of aqueous vapour and a diminution of the supply of oxygen, but in the absence of correct and sufficient information on the subject 40 years ago, ironsmelters ascribed some virtue to a blast as cold as circumstances permitted, because in the winter season as a rule they made more iron with less fuel than in summer, simply because

from one of our furnaces, so as to secure the presence of the whole of the solid constituents before analysing. It contained—

Soluble in water—

Loss in heating	10.46
Silica	1.37
Alumina	12.20
Lime	Tr.
Magnesia	Tr.
Chlorine57
Sulphuric acid59
Oxide of zinc	4.58
Carbonates of soda and potash	22.90
	<hr/> 52.67

Insoluble in water—

Silica	11.00
Alumina and oxide of iron	10.76
Lime	2.06
Magnesia	Tr.
Oxide of zinc	13.23
Carbonic acid	7.00
Alkaline salts	3.07
	<hr/> 47.17
	<hr/> 99.84

each stroke of their blast engine supplied them with more oxygen, and less carbon was absorbed in the decomposition of watery vapour than in summer.

Under these circumstances it is not surprising that Neilson's proposition to heat the blast before it entered the furnace was not favourably received, or that a considerable time elapsed before the value of his invention was recognized by practical men.

It is not my intention to detain you with any comparison between the nature of hot and cold blast iron, indeed, this would be a task beyond my power for want of the necessary data. There is no doubt that some of the best, if not the best, makes of iron in this country are produced by means of cold blast; but whether this excellence of quality is due to the temperature of the air or to the materials employed is a point upon which no opinion of any value can be formed until the same materials have been treated by both systems, and the results experimentally and practically examined.

The fact, however, that out of the four or five millions of tons of pig-iron annually produced in this empire, all but one or two hundred thousand tons are smelted by means of heated air, will be accepted as a proof of the soundness of Neilson's discovery.

The chief recommendation of the hot blast is the economy of fuel obtained by means of its use, and it is this attribute which possesses interest to ourselves as chemists, furnishing, as it does, a field of inquiry into the nature of the combustion and the appropriation of the heat in the blast-furnace.

In entering upon an explanation of the action of the hot blast, we must consent to lay aside those accounts which inform us that, immediately after its introduction, the mere heating of the air up to 320° F. (161° C.) enabled a smelter to reduce the consumption of coal for one ton of iron from $7\frac{1}{2}$ tons to $2\frac{1}{4}$ tons.

If it can be shown that the progress of smelting-science has been such as to reduce the consumption of coke in a furnace blown with cold air until it is within 10 or 11 cwt. per ton of iron of that used in a furnace supplied with air heated, not to 320° F. (160° C.) but to 650° F. (339° C.), this is the saving we are called upon to explain, and not five or six tons of coal, however instrumental the employment of hot blast may have been

in leading up to those general improvements which have benefited both modes of operating.

With the view of satisfying myself by personal enquiry what the consumption of fuel in furnaces fed with cold blast actually is, and for obtaining information on the process generally, I have recently visited the establishments of the Lilleshall Iron Company, in Shropshire, of the Blenavon Iron Company, and that of my friend Mr. Crawshay, in South Wales, and I cannot deny myself the pleasure of recording in this paper my grateful thanks for the unreserved access which was granted for the purpose of making the necessary experiments and observations.

Granting, then, for the present moment, that a furnace having its blast heated to 650° F. (339° C.), can make a ton of iron for 10 or 11 cwt. less coke than one driven with cold air, this extent of saving, moderate as it is when compared to the five tons of former days, requires some explanation, when it is remembered that the blast has the 650° F. (339° C.) of heat communicated to it by means of 5 cwt. of coal, of which I have ascertained that more than one half is wasted in the hot air apparatus,* so that practically you have the heat of about 2 cwt. of fuel burnt outside the blast furnace, effecting a saving of that burnt in its interior of 10 cwt. to 11 cwt.

The generally received opinion respecting the mode in which hot air effects the reduction in the consumption of coke is that a higher temperature is commanded in the furnace by its use than when cold air is employed, and, as Dr. Percy truly says in his recent work on metallurgy, "suppose a certain metal to require $1,000^{\circ}$ C. for its fusion, it might be subjected to 999° for ever without melting. Just so," he continues, "it may be in the blast-furnace with respect to the carburization of the reduced iron and certain other chemical actions, which moreover take place with slowness at one temperature, and with rapidity at another more elevated. In order to produce these actions in a furnace on cold blast, it is requisite to consume a much larger quantity of coal than in a furnace on hot blast. A few degrees of temperature may make all the difference." The Doctor goes on to explain cer-

* The temperature of the gases of combustion, leaving the hot-air stoves at the Clarence Works, was found to be about 1400° F. (760° C.), to which has to be added loss from radiation.

tain minor causes which may give rise to some saving, but in the end he admits that none of the answers which have been given as explanations of the theory of the hot blast are to himself satisfactory, and that a solution of the question is still wanting. Not as explanatory, but as a statement of a probable fact, Dr. Percy reminds us that inasmuch as for every ton of iron made, a larger quantity of coke is consumed when the furnace is driven with cold than with hot air, it is clear the number of units of heat evolved can have little to do with the matter, and that this being admitted, the inevitable conclusion is that *calorific intensity* must be concerned, and that the temperature of what may be designated as the most active part of the furnace must be higher with the hot blast than with the cold.

It is needless to trouble you with quotations from other authorities, who all appear to agree with this writer, although some of them quote other reasons than those assigned by him in support of the view just stated.

Let us consider how far this idea of increased calorific intensity accords with probability and with fact; and for this purpose it may be well to regard the subject in the first instance from the practical point of view.

It will probably be conceded that if the temperature of one furnace were greater than that of another, the fused materials from it, *i.e.* pig-iron and slag, should show some symptoms of the difference of temperature. Most of the cold blast iron smelters with whom I have discussed the subject during recent enquiries, and all of whom have also furnaces blown with heated air, appear to consider that the iron from the latter is the more fluid of the two. This, however, may be due to some difference in composition of the metal itself; for they all at the same time admitted, that so far as heat could be estimated by colour, there existed no reason for supposing the temperature of either slag or iron to be lower from a furnace driven by cold than from one supplied with hot blast. In company with our own furnace manager, Mr. Thompson, a gentleman of large experience, who assisted me in my observations, I certainly arrived at the same conclusion.

Again, experience and practice have demonstrated, beyond all question, that the production of different qualities of pig iron is determined by the temperature of the furnace—No. 1

being obtained when the working is at the hottest; indeed, so established a fact is this, that smelters are pretty well agreed among themselves as to the additional weight of coke which is required to raise their produce each number in the scale. Now this being the case, where, it may be asked, is the authority for supposing that the heat of a hot blast-furnace running, say No. 3 iron, is higher than that of a cold blast-furnace producing the same quality? Were the "calorific intensity" greater, as Dr. Percy supposes, one would imagine, from the law just alluded to, a higher quality of metal would be the result, as indeed happens whenever, from any cause, the heat is increased.

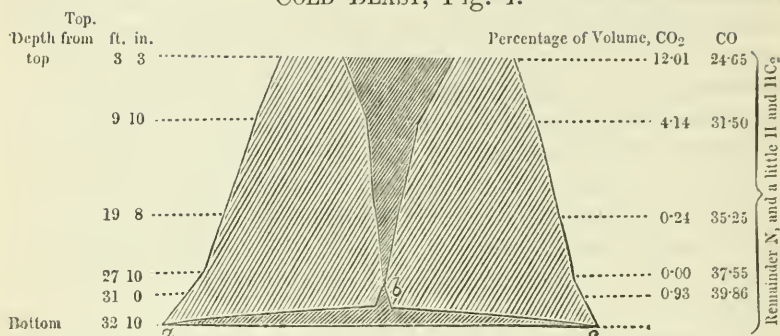
It is very true, that when a furnace is looked into at the tuyeres, one blown with hot-blast exhibits a dazzling white heat, whereas the large amount of cool air poured into a cold-blast furnace produces a tuyere which is more or less black; but are we entitled to consider this refrigeration more than local?

At no portion of the furnace, except at the top, does there exist less reason why the composition of the gases should experience more variation than near the region of fusion; for by this time all chemical change in the ore and flux has been accomplished. Neither is there any portion, with the exception above given, where an average sample is more easily collected, inasmuch as the sectional area of the furnace is much smaller and its condition generally more uniform than higher up.

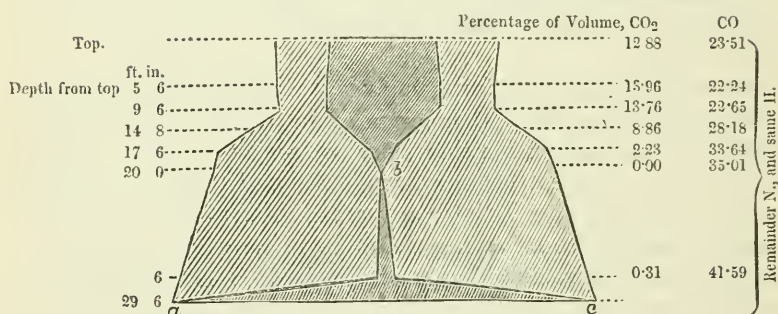
Now, the first effect upon the blast on its being admitted into the furnace is the conversion of its oxygen into carbonic acid, and the extent of space in which this change is effected may be accepted as an expression of the intensity of the heat produced in that space. On looking over the analyses of the gases of furnaces, I cannot find any justification for the idea that the oxygen unites more rapidly with carbon in hot than in cold-blast furnaces.

The same mode of showing the meaning which is intended to be conveyed has been pursued as when describing the composition of the gases of the furnace, viz., by diagram. The first one shows the carbonic acid and carbonic oxide in a cold blast, and the other in a hot-blast furnace, with air heated to 190° C. (374° F.), both at Clerval, in France, using charcoal, the analyses being those of Ebelmen.

COLD BLAST, Fig. I.



HOT BLAST, Fig. II.



In the diagram No. 1, cold blast, the carbon vapour from existing entirely as carbonic acid at the tuyeres, by the time it travels 22 inches, exists only in this form to the extent of .93 per cent. of the total gases, and, by the time 5 feet from the bottom is reached, there is no longer any carbonic acid present. In other words, the oxygen of the blast has in this space been all converted into carbonic acid and afterwards changed into carbonic oxide.

In the case of the hot-blast furnace, a distance of 3 feet from the bottom shows 0.31 per cent. of carbonic acid, and a height of $9\frac{1}{2}$ feet has to be travelled before it disappears; so that undoubtedly, so far as temperature can be judged of, by the smallness of the space in which perfect oxidation and subsequent reduction to carbonic oxide is effected, the cold-blast furnace would appear to be the hotter of the two. Certainly the dia-

grams in which the relative dimensions of these spaces are expressed by the dark shading in each case comprised within *a, b, c*, do not exhibit any reason for supposing the temperature of the zone of fusion is higher with the hot blast than that of cold; whereas some grounds have been given to show that the difference, if any, is very trifling.

Permit me to invite your attention, with a view of endeavouring to ascertain whether the mode of action of the hot-blast cannot be explained upon different grounds. Before doing so, it may be questioned whether the supposed calorific intensity, suggested by Dr. Percy, as being required for the carburization of the reduced iron and some, at least, of the other chemical actions may not be omitted in the enquiry; for, if the views laid down in this paper are correct, most of the chemical changes on the materials have been effected in a much cooler part of the furnace.

It will be recollected that we started upon this enquiry with supposing that the heat from 2 cwt., or thereabouts, of fuel, which we will, for simplicity's sake, assume to be pure carbon, represents the heat thrown into a furnace by means of the blast being heated to 339°C . (650°F). In practice, we are pretty near the truth in accepting as a fact, that an estimate of the heat developed by the blast on the coke is obtained by considering its oxygen converted into carbonic oxide; for although at the instant of its admission carbonic acid is generated, this substance is almost as rapidly converted into carbonic oxide by the action of the incandescent coke. But in the hot-air stoves the 2 cwt. of carbon is converted permanently into its highest state of oxidation, and, taking the units of heat as 2221°C . for burning carbon to carbonic oxide, and as 7900°C . for burning carbon to carbonic acid, the 2 cwt. burnt in the stove will represent 7.11 cwt. of carbon burnt in the furnace, or, say, something like $7\frac{1}{2}$ cwt. of coke.

In round numbers, therefore, we may consider $7\frac{1}{2}$ cwt. of our saving of the 10 or 11 cwts. to be accounted for, leaving still $2\frac{1}{2}$ to $3\frac{1}{2}$ cwts. for further investigation.

Now, let us assume that the coke required is 40 cwt. for the ton of cold-blast iron, and into the furnace, blast heated to 339°C . (650°F .) is suddenly introduced, which is, as we have seen, equal in calorific power to $7\frac{1}{2}$ cwt. of coke, so that so far as a mere question of heat is concerned, something like $47\frac{1}{2}$ cwt. of

coke is being applied to the production of a ton of metal for which 40 cwt. will suffice.

A common yield of calcined clay ironstone is 40 per cent., so that 50 cwt. are required for a ton, to which has to be added, say 12 cwt. of limestone. The "burden," then, for one ton of cold-blast iron would be—

Coke, 40 cwt.; calcined ironstone, 50 cwt.; limestone, 12 cwt.

But by the addition of the equivalent of $7\frac{1}{2}$ cwt. of coke, these proportions will require a corresponding modification, and a ton of iron will be represented by—heat in blast, equal to $7\frac{1}{2}$ cwt. of coke; coke reduced by this addition of heat in the blast to $32\frac{1}{2}$ cwt.; calcined ironstone and limestone as before, viz., 62 together.

But what is the effect on the furnace itself by such a change in the proportion of its contents. To answer this, let us imagine a furnace with a capacity of 6,000 cubic feet.

The weights of the materials used at the Clarence Works have been carefully ascertained, and, as charged into the furnace, are—

Coke, .234 cwt. per cubic foot as contained in the barrow.

Calcined iron-stone, .624 cwt. per cubic foot as contained in the barrow.

Limestone, .706 cwt. per cubic foot as contained in the barrow,

or, taking the average of the two last together, in the proportions they are used, .640 cwt. will represent a cubic foot.

It was further determined that the weight of material in a furnace, before being lighted, was such as to indicate a compression of something like 25 per cent., so that a furnace of 6,000 cubic feet would contain 7,500 cubic feet of materials as measured in the charging barrows.

By these figures it would appear that such a furnace working on cold-blast would contain—

Coke	56 tons
Calcined ironstone and limestone ..	87 „
	<hr/>
	143 „

but introduce the air heated so as to reduce the coke to about 30 cwt. to the ton of iron, and the furnace would contain of

Coke	50 tons
Calcined ironstone and lime	103 „
	<hr/>
	153 „

Neither of these two sets of figures really represents what is contained in a blast furnace at any one time when filled and in working order. In the case of the hot-blast furnace, 103 tons of ironstone and limestone represents 24 hours' working, whereas, as is well known, it requires something like 36 hours, at the usual rate of driving, to pass the entire contents through such a furnace. The estimate is based on what 7,500 cubic feet will contain of cold materials, whereas when the furnace is in full operation, the coke loses considerably in weight before it reaches the tuyeres, and the other materials become greatly condensed as they approach the seat of fusion.

It would be almost impossible to ascertain to what extent these figures become modified by the action of the heat when the furnace is in blast, or what the effect of the altered proportions would be on the temperature of the ascending gases.

To obtain the exact figures for this, we ought to have the specific heat of all the various materials in the furnace; and it would be equally difficult to ascertain what the specific heats of the contents of the furnace really are during the process of smelting, as it is difficult to ascertain the temperature of the different portions of the interior of a furnace.

Schinz has shown, in a recent work, how rapidly the specific heats increase with rise of temperature. According to his researches, the following list shows the change of specific heat with elevation of temperature:—

At	Coke.	Limestone.	Lime.	Iron ore.	Iron.	Slag.
100° C.	·157	·166	·216	·171		
250° C.	·186	·273	·233	·185		
500° C.	·234	·451	·260	·209		
750° C.	·283	·628	·287	·233		
1000° C.	·330		·314	·257	·152	·259
1500° C.	·428				·184	·322
2000° C.	·525				·216	·384

Without any information to guide us as to the exact condition, chemically speaking, of the contents of the furnace, or the rate at which they lose weight and acquire heat, it would be

mere guess-work to estimate the number of units of heat intercepted by the materials under treatment.

That the withdrawal of so many cubic feet of coke, and the substitution of substances nearly three times its weight, and with a mean specific heat rather higher than that of the coke itself, must permit a more perfect absorption of heat from the ascending current of gas is obvious.

In illustration of this, an experiment made at the Clarence works of this may be quoted. Through a pipe 12 inches in diameter and 6 feet high, a given volume of air, heated to the melting point of lead, was passed.

The pipe was filled with coke properly dried, and afterwards with calcined ironstone, and then limestone. The power of intercepting heat from the same volume of air is expressed by the following numbers:—

For Coke	100
„ Calcined ironstone	188
„ Limestone	144

Looking at the complicated nature of the problem, it appears as if there is no alternative left but to ascertain the actual amount of heat carried off in the escaping gases, after they have performed their work in the furnace, and this during a whole day was done most carefully at the Cyfarthfa works at a hot-and-cold-blast furnace.

The mode of procedure was as follows:—To ascertain the temperature of the gases, a pyrometer, made by Kraus of Paris, was plunged into the gases where they left the the furnace, and occasionally an observation was taken by means of apparatus supplied by Mr. C. W. Siemens, consisting of a copper cylinder, which, being immersed in the gases, indicated their temperature by the amount of heat it conferred on a given quantity of water. Both of these instruments are open to the objection of requiring time, so that in cases where the temperature is constantly changing, neither gives results which are strictly correct. To obviate this difficulty I constructed another pyrometer, which, though liable to some irregularity, possesses the advantage of being much more immediate in its indications. It was simply a copper tube, about 3 feet long and 1 inch diameter, closed at the lower end and screwed into a Bourdon's pressure guage, so that it was hermetically tight. The expansion of the

air by increasing the pressure enabled me to read off minute variations almost the instant they took place.

To estimate with strict correctness the heat carried off with the gases, an analysis of samples extending over some hours would have been required, both for the purpose of calculating the quantity and the specific heat. This was not in my power to do, and in consequence the composition of the escaping gases has been assumed as being the same as those given off by a furnace of nearly the same dimensions at the Clarence works. It is believed that any difference in respect to this will not seriously affect the results of the calculation.

The gases were assumed to contain according to weight—

CO_2 9 CO 32 N 59 = 100			
The C in CO_2 = 2.45	C in CO = 13.71	= total C 16.16	
O „ = 6.55	O „ = 18.29	„	O 24.84
<hr/>		<hr/>	
Total CO_2	9.00	total CO	32
		total C & O	41.00
Coke used per ton of iron was cwt. 34.80			
Deduct ash 5 per cent.		1.74	
HO (weather was wet) 5 „		1.74	
For combination with iron		.74	
		<hr/>	4.22
			30.58
Carbon in limestone			2.12
		<hr/>	
Total carbon going off in gases			32.70

With the composition of the gases given above this carbon will be volatilized in the following state as—

CO_2	4.96 cwt.		
CO	27.74	„	
<hr/>			32.70
C 4.96 for conversion to CO_2	requires O		13.23
C 27.74 „	CO	„	O 36.99
<hr/>		<hr/>	
32.70	Total	O	50.22

But in the materials themselves there is—

O in the CO_2 of the limestone (viz.,			
17.66 cwt. per ton iron) =		5.65	cwt.
O in 48.43 ores (part of Fe being as			
FeO)		7.35	„
		<hr/>	13.00

Leaving to be supplied by blast of O 37.22

The total weight then of the gases would be—

Carbon.....	32.70 cwt ^s .
Oxygen ..	50.22 „
Nitrogen accompanying 37.22 O of blast	124.60 „
Water in coke 1.74, water in ore 2.19 ..	3.93 „
	<hr/>
	211.45

We have as total weight of gases—

C	4.96 + O 13.23 = CO ₂	18.19 cwt ^s .
C	27.74 + O 36.99 = CO	64.73 „
N		124.60 „
HO		3.93 „
	<hr/>	= 211.45 „

The mean temperature of these gases as they left the furnace was ascertained to be 445° C. (833 F.)

By multiplying these weights by their various specific heats and temperature we have—

$$\left. \begin{array}{l} \text{CO}_2 \ 18.19 \times .212 \times 445^\circ \\ \text{CO} \ 64.73 \times .288 \times 445^\circ \\ \text{N} \ 124.60 \times .275 \times 445^\circ \\ \text{HO} \ 3.93 \times 1.0 \times 445^\circ \end{array} \right\} = 26967$$

And this divided by 2221 units of heat, burning C to CO, gives—12.16 cwt. carbon, or say 12.76 dry coke, as going off with the escaping gases from the cold-blast furnace.

In the case of the hot-blast furnace, with air heated to 320° C. (608 F.), the calculations stand thus—

Coke used per ton of iron was 26.74 cwt ^s .	
Deduct ash in coke 5 per cent.	1.33
Ditto HO in do. „	1.33
Ditto C combined with iron	.74
	<hr/>
	3.40 „
	<hr/>
	23.34 „

Lime was added in its caustic state, hence there is no carbon to include from this source.

Upon the same basis as the previous calculation the carbon will be given off in the gases as—

CO ₂	3.53 cwt ^s .
CO	19.81 „
	<hr/>
	23.34

C 3.53	requires for conversion to CO_2 — of O	9.41
C 19.81	„	CO — of O 26.41
<hr/>		
23.34		35.82
Less O in the ores, Fe partly existing as FeO		8.12
<hr/>		
Leaving O to be supplied by blast	27.70

Total weight of gases will be—

Carbon	23.34
Oxygen	35.82
Nitrogen accompanying 27.70 O		92.73
Water in coke 1.33, and ore 1.73		3.06
<hr/>		
		154.95 cwts.

The mean temperature of these gases was ascertained to be 477°C . (891°F .), and their estimated constitution would be as follows:—

C 3.53 + O 9.41	= CO_2	12.94
C 19.81 + O 26.41	= CO	46.22
	N	92.73
	HO	3.06
<hr/>		
		154.95 cwts.

By multiplying these weights by temperature and specific heats we have—

CO_2 12.94	$\times .212$	} $\times 477^\circ = 21274$
CO 46.22	$\times .288$	
N 92.73	$\times .275$	
HO 3.06	$\times 1.00$	

This divided by 2221 = 9.57 cwts. carbon, or dry coke 10.04.

Now as the heat escaping from the cold blast furnace represented in coke for each ton of iron 12.76 cwts.
Whereas with that on hot blast it is only 10.04 „

It follows there is escaping from the cold blast

* The fact that very different materials were employed in the two furnaces which were examined, prevents a strict comparison between their respective temperatures being instituted. All that can be done is to ascertain in both cases the actual amount of heat escaping.

furnace, above that going off from the hot, heat
equal to coke..... 7.72 cwts.

We have in consequence the total saving of coke as follows:—

1st. By use of blast heated as formerly stated	7.50 cwts.
2nd. By diminution of loss of heat in the escaping gases	2.72 „
	<hr/> 10.22 „

Which accords with the saving given as effected by the use of 5 cwts. of coal for heating the air, of which only about 2 cwts. were really available.

It may be interesting to compare the duty of the two different furnaces, by deducting the heat carried off by the waste gases, and that required for melting the slag, which latter varies of course in amount according to the minerals used. In estimating the fuel required for this latter object, Vathaire's figures of 550 units per kilogramme of slag is accepted as the basis of calculation.

The hot-blast furnace in Wales stands thus, making white iron—

Coke used per ton of iron.....	26.74 cwts.
Heat contained in 120 cwts. of blast at 320°	
$120 \times .287 \times 320$	
<hr/>	<hr/>
2221	= carbon 4.95 = coke 5.16 „
	<hr/> 31.90 „

Heat escaping with gases—

As formerly calculated = carbon 9.57

Melting 23 cwt. slag, do. 5.70

—— 15.27 = coke 16.04 cwts.

Leaving for reduction and fusion of metal, loss

from radiation, &c. 15.86 „

The cold-blast furnace in Wales exhibits the following results, also producing white iron:—

Coke used per ton of iron as formerly given ..	34.80
Heat 37° C. (100° F.) contained in blast pro- duced by compression in blast engine	
$162 \times .287 \times 37 \div 2221$78
	<hr/> 35.58

Heat escaping with gases as formerly estimated =	
carbon	12·16
Melting 30 cwt. of slag do.	7·43
	———— 19·59 = coke 20·49
Leaving for reduction and fusion of metal,	————
loss from radiation, &c.	15·09*

Let us test by another method this mode of calculation. Suppose two furnaces of such dimensions, and using such a kind of mineral that for producing the same quality of iron the consumption was 30 cwt. per ton of iron for hot blast, and 40 cwt. for cold blast.

For the hot blast furnace we have coke....	30 cwts.
And with the air at 800 F. (426 C.) there will be heat equal in coke to about.....	8 „
	————
	38 „
Deduct for heat carried off by gases some- thing like.....	9 „
	————
Leaving for reducing iron fusing it and the slag, loss by radiation, &c.	29 „
	————
In the case of the cold blast furnaces the coke is taken at	40 „
Added with blast by compression heat equal in coke to about	1 „
	————
	41 „
Carried off by gases say	12 „
	————
Leaving for reduction of iron, &c.	29 „

Imagine now that instead of introducing with the blast the heat of 8 cwts. of coke, an equivalent of which and more escapes at the top of a low furnace, measures were taken to prevent this source of loss, which is something like 12 cwt. of coke in the case of one blown with cold air. This could be done by adding something to the height, and thus cause the highly heated gases to yield up the greater portion of their heat to the additional materials contained in this increase of size. If the temperature of

* The iron from this furnace was somewhat inferior in quality to that from the hot blast furnace, which may account for the difference between 15·86 and 15·09 cwts.

the gases from a cold blast furnace was such that it represented 2 instead of 12 cwts. of coke, a clear saving of 10 cwts. would be effected by the change, or the 40 cwts. of coke per ton of iron might be reduced to 30 cwts., for we would have 30 + 1 cwt. for heat conveyed in

The blast =	31
Less carried off in gases	2

Leaving .. 29 for actual

furnace work.

Now, this is exactly what has been done at the Lilleshall Iron Works. Furnaces formerly 50 feet high have been raised to 71 feet in height, and the consequence has been, that those of the latter dimensions, blown with cold air, are making iron for the same quantity of fuel used by hot blast furnaces of the former size, viz., 50 feet.

Unfortunately, the mode of construction is not such as to permit a verification of the actual heat going away from each; but there is little doubt that were this done, we should see that the sum of heat introduced by coke and blast, *minus* that escaping, gives in both cases the same result to represent work actually performed.

Of course, all this forms no argument against the economy of the hot blast; because from furnaces of 48 and 50 feet, blown with heated air, something like 10 cwt. of coke escapes in the gases—a loss which has been reduced to something under one half of this by adding 30 feet to their height; indeed, it was with hot-blast furnaces that the great advantage of increased height was first demonstrated.

It is almost needless to say that there are, in connection with the blast-furnace, many other questions of a highly interesting nature in a scientific point of view, as well as most important regarded as matters of practical economy, which the length of time I have occupied your attention forbids me to enter upon. Such are, the actual heat given off by the combustion of the fuel compared with the real effect produced, together with many others. I have, instead of going into these, preferred submitting for your consideration views connected with the subject of iron smelting, which, so far as I know, differ in some respects from those previously expressed.

The President, in inviting discussion, said: There is scarcely any branch of manufacture which requires so many various qualities of a rare and high kind as this particular one in which Mr. Bell is pre-eminent, and, certainly, among ironmasters there is none equal to himself in the combination of those various qualities. His scientific skill and industrial vigour have led to the construction of iron furnaces which are unsurpassed in the perfection of the operations which pertain to them. The subject is one so complicated that Mr. Bell's views will be considered exceedingly valuable in relation to it, and, certainly, all will feel interested in having so full and so masterly an exposition from himself in this matter.

Mr. Siemens: With regard to the saving effected by hot blast, a great deal of controversy has taken place, and I am very glad to see that Mr. Bell has really tackled the question by reducing it to figures. At first sight it appears strange that the combustion of 2 cwts. of carbon added to the blast should save 10 cwts. of coal in the blast-furnace; but a little consideration would, I think, bring us already to this conclusion. If the result of combustion were carbonic acid only, then every 6 lbs. of carbon added in the shape of heat to the blast would necessarily save 14 lbs. in the furnace, that being the proportion of heat developed in burning carbon into carbonic oxide and into carbonic acid; but we find the result of combustion is not carbonic oxide but a mixture of carbonic oxide and carbonic acid. It may be assumed to be, in a furnace worked with hot blast, one-fifth carbonic acid and four-fifths carbonic oxide; and, if we take these proportions, we shall find that the effect of 1 lb. of combustion outside the furnace would probably produce a saving of 4 lbs. inside the furnace. But why is the saving greater? If we suppose that a mixture of air, reduced ore, and carbon, comes down the furnace, and is met by the blast, the first action is complete combustion into carbonic acid; but almost simultaneously with that action the reducing action, or the absorbing action of the carbonic acid upon carbon, takes place also. The carbonic acid is reduced to carbonic oxide, and this reduction is accompanied by a great refrigerating effect. If cold blast is used, there must be a larger proportion of carbon present with the ore, and there must be a larger surface of carbon at once exposed to the carbonic acid formed in order to effect its reduction. It has been determined

practically that a cold-blast furnace not only works hotter at the top, but that the proportion of carbonic acid is greater in the case of a hot than of a cold-blast furnace; it would therefore follow that the hot blast has not only produced a higher temperature at the bottom, but reduced a mixture of carbonic oxide and carbonic acid, giving a larger margin of heat developed, or less refrigerating action introduced by the formation of carbonic oxide. Perhaps Mr. Bell will be kind enough to tell us whether, on raising the temperature of the blast, the proportion of carbonic acid gas at the top of the furnace is not increased.

Mr. Bell: If you had a hot and cold-blast furnace working together, irrespective of the results, with the same quantity of fuel and the same quantity of ore, then the comparison Mr. Siemens is making would be a perfectly true one. But it happens to be the case that, upon a comparison of the Clair-vale furnace, blown with a hot and with a cold blast, you find the volume of carbonic acid in the cold is considerably greater than that in the hot.

Dr. Paul: If we compare two furnaces, one worked with cold blast, and burning fuel at the rate of two tons for each ton of iron produced, and a hot blast furnace worked so that the consumption of the fuel is at the rate of only one ton for each ton of iron produced, we must remember that, in fact, the largest proportion altogether of the materials passing through those furnaces in both cases is the air by which the combustion is supported. Therefore, taking it for granted that in both cases the discharged gases go away at the same temperature, we have in the one blast-furnace twice the amount of gaseous material passing through the furnace, and twice the quantity of heat being carried off in that escaping gas. Therefore it is evident that the quantity going away to waste in the cold-blast furnace is twice as great as in the hot-blast furnace; and if we had the waste twice as much in the one case as it is in the other, it is very evident that in the hot-blast furnace there must be very considerable saving.

Captain Noble: With respect to the ratio between carbonic acid and carbonic oxide in the waste gases, Mr. Bell has found that, within a very short time, and while apparently the furnaces are working precisely the same, there is a very great difference in their ratio. I entirely agree with what Mr. Bell

has said, and I believe very little in the analyses of tunnel-head gases. The analyses of gases taken from pipes are, I believe, entirely fallacious. It is almost impossible to believe that ratios in crooked lines, like what we see on the diagram, can really exist in a furnace, and it is very evident that when we take gas from a furnace by means of a small pipe, the nature of that gas will change very much in accordance with the last substance with which the gas has come into contact—whether it be coke, for example, or whether it be ironstone. I have had occasion myself recently to make an investigation with reference to the determination of the number of units of heat produced in a furnace, and what became of them. In so doing, I have endeavoured to trace the number of units of heat that go away with the tunnel-head gases, and which are re-produced when the tunnel-head gases are burnt, and so on. And, finally, I have worked it out in the work that is done by the engines and other means. The great variations that Mr. Bell has found in his analyses of the gases from the pipes is entirely confirmed in another way, and that is, by the amount of water vaporized. In the space of three or four hours the amount of water vaporized varied most enormously, and, if I remember right, Mr. Bell found a variation in the ratio of the carbonic acid amounting to something like 20 per cent. of the whole amount. The ratio also varies much in the different furnaces.

Mr. Crossley: It is certainly surprising to find that iron absorbed carbon at so early a stage in the furnace. I have passed pure carbonic oxide over pure sesquioxide of iron, and I never noticed any deposition of carbon; and I am rather afraid that, in the case of Mr. Bell, the calcined stone had not been fully calcined in the interior of the stone, and perhaps the carbon which he obtained in the deposit was the carbon which was left in the stone. Mr. Bell has also told us something which I consider very interesting in reference to the proportion of limestone that may be used in a furnace, and he stated that the smaller the quantity of limestone used, the larger the percentage of sulphur which comes off in the pig-iron. We tried some years ago some experiments in which we used $3\frac{1}{2}$ cwts. of limestone, 7 cwts., and, I believe, 14 cwts., and we have found that the silicon and the sulphur in the iron came off in larger quantities in the iron where the smallest quantity of limestone

was used, and there was a smaller proportion of metallic bases in the pig-iron produced from the smallest quantity of limestone.

Mr. Cochrane : I shall be glad to offer a few observations on the subject of hot blast, which has been rather a pet subject with me for a great many years. I believe it is an admitted fact, that the colder oxygen is, and, of course, the more dense it is, the more intense is the action of combustion due to that oxygen, and that there is no advantage in warming it. But not so, I believe, with nitrogen, and, of course, with the mixture of atmospheric air. I think that the question of heating that mass of nitrogen has been rather overlooked in the paper; and, not only has a large amount to be heated in the furnace, but, I believe, a greater weight of nitrogen has to be heated for every ton of iron that is reduced. Mr. Bell has alluded to a dark appearance before the tuyere. It is notorious that this dark appearance extends, in many instances, to a long tube, right into the centre of the cold-blast furnace; and that is really part and parcel of the heating apparatus which enables the blast to be delivered in the cold-blast furnace at the requisite temperature for the quality of iron required. Hence it needs the element of time of combustion to be taken into account, or not the time of combustion rather, but that the material—the coke—is, in being burnt, higher in a cold-blast furnace, by reason of the time required for heating all the nitrogen, and so on, than is the case in a hot-blast furnace, where you start with temperature of, we will say, 1000° F., and where there is no longer any necessity for heating that blast inside the furnace. The zone of fusion is spread lower down the tuyeres, and so, *pro tanto*, you gain in height of furnace.

Mr. Bell : I will not take up many minutes in replying to the questions which have been put before us. One point raised was as to the greater volume of gases escaping from a cold-blast furnace than from a hot. Well, I have not given figures on that point, because, as I stated before, I have intruded too long upon the company already. But it was, of course, impossible to ascertain the quantity of heat escaping by the gases at a certain temperature, unless I had known the quantity of gases escaping, which was a necessary element in the calculation. With respect to the observations of Mr. Crossley, with regard to the possibility of the carbon in the ironstone being

the cause of the deposition of the carbon in the iron, I would remind him that a certain temperature was required. If this carbon was deposited from the carbonic acid already existing in the iron ore, how did it happen that it never found its way there, when it was exposed merely in a blast-furnace having the escaping gases going out at a temperature something like melting lead? There was an invariable connection between the temperature of the escaping gases and the appearance of this carbon. With regard to my friend Mr. Cochrane, all I can say is this, that I am not prepared to dispute whether it is better to heat the oxygen or better to heat the nitrogen. But this appears to me quite certain, that as you look upon the blast as a mere vehicle for conveying the heat, it is a matter of perfect indifference whether the heat is carried in by 8 lbs. of oxygen or 14 lbs. of nitrogen.

I have made diagrams, not from imagination, but based upon actual analyses of the gases, to show that, at a given point, the whole of the oxygen of the blast is absorbed, and whether the blast went in hot or cold appeared to make no difference. The carbonic acid was as readily reduced to the condition of carbonic oxide in the hot blast as in the cold. The figures before you illustrate quite truly the temperature of the gases as they were coming from two furnaces and at different periods of the day, and they merely show the irregularity of action of all blast furnaces, and how impossible it is, from a few observations, to draw any general expression as to their action.

The President: I am sure we must feel greatly indebted to Mr. Bell for his exceedingly able exposition. Two or three things have certainly become clear; in the first place, that a saving must be effected by replacing as much as possible that imperfect combustion which takes place in the furnace by the more perfect combustion which may be effected outside the furnace when it is applied to heating the blast. That there must be a saving in that way is obvious. I remember it was some years ago that Mr. Siemens drew my attention to that as a necessary source of saving in the utilization of hot blast, and certainly it was from him that I first learned that circumstance as bearing upon it. Another exceedingly weighty circumstance which we now, at all events—or I for my own part—learn to consider in relation to this, from Mr. Bell, is the

difference of the charge of the furnace under the two conditions. If we have less coal present in the furnace in proportion to the ore, or, in other words, if we have more ore in proportion to the coal, we have a greater quantity of good heat-absorbing substance. That tells in two ways, as Mr. Bell has exceedingly well shown, not only by absorbing the sensible heat of these two gases, but also by burning some of the carbonic oxide which would otherwise have escaped unburnt. I think it is of particular interest that Mr. Bell has proved that the gases at the temperature of combustion, at which they usually escape, are capable of reducing a great deal of oxide of iron; and that does seem to me to point to a direction in which we may effect improvement in these furnaces.

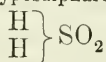
XIX.—*On the Constitution of Hyposulphurous Acid.*

By C. SCHORLEMMER.

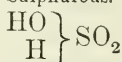
(Read May 20th, 1869.)

IN a paper on the Synthesis of Formic and Hyposulphurous Acids, published in the Journal of the Chemical Society, N.S. v., 291, Dr. Dupré describes some experiments, from which he infers that formic acid and hyposulphurous acids have an analogous constitution, hyposulphurous acid being, in fact, formic acid in which the carbon is replaced by sulphur, and *vice versa*. He finds a support of this view in the observation of Rose, that no hyposulphite is capable of existing which does not contain at least one atom of hydrogen, and he proposes, therefore, to reduce the molecular weight of hyposulphurous acid to one half. Dr. Odling has lately expressed similar views;* he also advocates the halving of the molecular formula, and considers hyposulphurous acid as a hydracid, in which only one atom of hydrogen is replaceable by a metal; sulphuric acid being an oxyacid and sulphurous acid standing between the two.

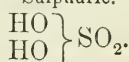
Hyposulphurous.



Sulphurous.

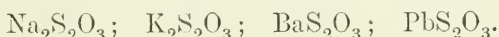


Sulphuric.

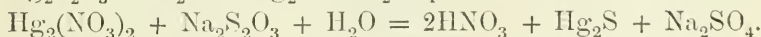
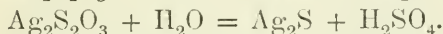
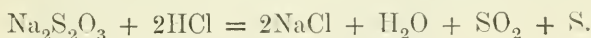


* Journ. Chem. Soc., ser. 2, vol. vii, 180.

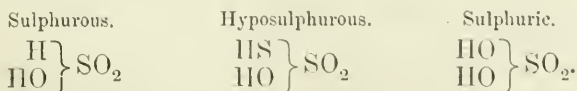
From this it appears not to be well known that Rose's statement, that hyposulphites containing no hydrogen do not exist, is incorrect. This was shown by Pape,* who found that all the hydrogen is present in the form of water of crystallisation, which, by taking proper care, can be expelled completely, without the salt undergoing decomposition, the only difficulty being that the temperature at which the last portion of the water is driven off is only a few degrees below that at which decomposition begins. Thus, the sodium, potassium, and barium salts can be obtained quite anhydrous by heating them up to 215° C. At 220°—225°, or only 5° higher, the salts begin to decompose, with separation of sulphur. The lead-salt loses all its water at 100°, but only at a few degrees above this temperature it begins to blacken. The formulæ of these salts are, therefore,



Moreover, there are other reasons which show that the molecule of hyposulphurous acid contains two atoms of sulphur. In a great many of its reactions it splits up in such a way that the atom of sulphur which was previously contained in the sulphur dioxide remains in the oxidized state, whilst the other atom separates as free sulphur, or as a sulphide.



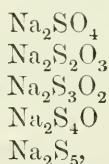
From these reasons it follows that we must retain the old formula for hyposulphurous acid, and consider it, as Dr. Odling first proposed fourteen years ago,† as sulphuric acid in which one atom of oxygen has been replaced by sulphur, both being derived from sulphurous acid, the former by adding to it one atom of sulphur, and the latter by the addition of one atom of oxygen.



* Poggendorff. Ann. cxvii, 408.

† Quart. Journ. Chem. Soc., vii, 8.

Dr. Odling referred to the discussion which followed the paper by Professor Stokes, "On a certain reaction of Quinine,"* in which it was shown that, as a general rule, the halogen salts of quinine, or those salts in which the quinine (or the quinium) is not directly combined with oxygen do not manifest fluorescence, whereas such salts as the sulphate and nitrate, which are essentially oxygen salts, do exhibit fluorescence. But there is a remarkable exception in the case of the hyposulphite, which, though ordinarily regarded as an oxygen salt, is not at all fluorescent. With reference to this point, he (Dr. Odling) ventured on that occasion to remark that it was possible that the compounds of hyposulphurous acid might be, after all, not oxygen, but halogen salts; and in favour of that view, he mentioned the observation of Rose, quoted in Mr. Schorlemmer's paper, not being then aware that this observation had been refuted. On the present occasion, he would like to call to mind the different views which had been put forward with regard to the hyposulphites. Looking to empirical formulæ only, sulphate of sodium is represented as Na_2SO_4 . The pentasulphide of sodium has the formula Na_2S_5 in which the S_5 may be taken to correspond with the S and the O_4 of the sulphate. Between these there might be three intermediate salts, making the series,



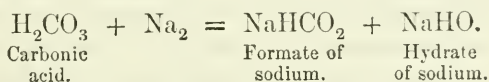
a series which appears very natural, and likely to exist. The first of the intermediate salts, viz., $\text{Na}_2\text{S}_2\text{O}_3$, is the ordinary hyposulphite of sodium. The second is described in Sir Robert Kane's "Manual of Chemistry," where it is said to crystallise with the same number of atoms of water as the hyposulphite, and to be isomorphous therewith. The third intermediate compound, $\text{Na}_2\text{S}_4\text{O}$, does not appear to have been obtained.

If now we oxidize sulphite of sodium, Na_2SO_3 , we obtain the sulphate, Na_2SO_4 ; and if instead of oxidizing it we sulphurize it, we convert it into the hyposulphite $\text{Na}_2\text{S}_2\text{O}_3$:

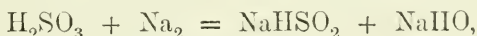
* Page 174 of this volume.

there is, therefore, an analogy between the sulphate and the hyposulphite, both in the ultimate formulæ and in this particular mode of formation.

On the other hand, Professor Kolbe succeeded in making formic acid by reducing carbonic acid with sodium, thus:—



This reaction appears at first sight very similar to the ordinary reaction by which a hyposulphite is obtained by the action of metals on sulphurous acid. The hyposulphite can be produced readily by dissolving zinc or iron in sulphurous acid; and if sodium were used, as in Professor Kolbe's reaction, a result would be obtained which might be expressed by the equation,



the caustic soda remaining combined with the excess of sulphurous acid employed. This fact led Dr. Dupré to form the opinion that formic and hyposulphurous acids are analogous compounds. He (Dr. Dupré) made several experiments by acting upon carbonates with carbon, and the results of these experiments induced him to believe that he actually produced formic acid; but these experiments, as Dr. Dupré himself acknowledged, could not be considered as altogether conclusive. With regard to formic acid, all experimental evidence tends to show that, in this acid, the carbon is united with oxygen, with hydrogen, and also with oxygen already combined with hydrogen, being, in fact, represented by the formula $\text{H}(\text{HO})\text{CO}$. But if it be right to say that hyposulphurous acid is not an oxygen acid, it must be represented by the formula HHSO_2 , in which both the hydrogen atoms are directly combined with sulphur. In favour of this latter view, Professor Stokes, on the occasion above referred to, adduced the exceptional fluorescence of the quinine salts of hyposulphurous acid, and some other reactions which will be found in his paper;* and he (Dr. Odling) supplemented those remarks by referring to the singular habits which the hyposulphites have of forming double salts exactly analogous to the double

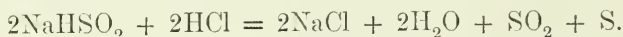
* Page 178 of this volume.

chlorides, for example, the double hyposulphite of silver and sodium, and the double hyposulphite of gold and sodium.

The reactions adduced by Mr. Schorlemmer, in which hyposulphurous acid shows so great a tendency to split up in such a manner as to yield one atom of sulphur still in the oxidized state, while the other makes its appearance as free sulphur, or as a sulphide, appear to him (Dr. Odling) as equally explicable on either formula. Taking, for example, the reaction with hydrochloric acid, we have, on the one view, (Mr. Schorlemmer's),



and the other,



The tendency of a hyposulphite to furnish a sulphate and a sulphide is strictly parallel to that of a hypophosphite or phosphite to yield a phosphate and a phosphide. Moreover, the mode of formation of hypophosphites is analogous to one mode of formation of hyposulphites.

With regard to the molecule of water in the hyposulphites, Dr. Odling said that if we represent hyposulphite of sodium according to the older view, we have the formula $\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$; he, however, preferred to write it 2NaHSO_3 . The salt retains its molecule of water with great firmness, requiring a heat of 215° to drive it off. The sodium, silver, and barium salts also require this unusually high temperature to dehydrate them. This, however, does not prove absolutely that the molecule of water in question is different from water of crystallisation, though it is in favour of that view; and the reaction may be precisely similar to that by which at a sufficiently high temperature two molecules of acid sulphate of sodium, 2NaHSO_4 , lose a molecule of water to furnish the salt $\text{Na}_2\text{S}_2\text{O}_7$. He had said, relying upon Rose's statement, that it was impossible to drive off the corresponding molecule of water from a hyposulphite; but now, corrected by Mr. Schorlemmer, he would merely say that was difficult.

Dr. Odling concluded by saying that the question is one on which he retains his mind quite ready to bend in either direction, as fresh facts may arise; but that at present he does not think that there are sufficient facts to enable us to decide the question absolutely either one way or the other.

The President expressed his opinion that there were two or three points brought forward by Mr. Schorlemmer which were entitled to some weight. First, there is the tendency of hyposulphurous acid to form double salts. Now, among the characteristics of bibasic acids, this tendency is, as a rule, one of the most conclusive, and he (the President) thought that, in the case under consideration, it ought to have considerable weight in favour of the bigger formula. With reference to the decomposition of hyposulphurous acid into sulphur and sulphurous acid, it occurred to him that there is a difference in degree between regarding this decomposition as resulting from the splitting up of one molecule, and regarding it as proceeding from a reaction between two molecules. We know, for example, that water is much more easily eliminated by heating a bibasic acid than by the mutual action of two molecules of a monobasic acid; and there are other cases which would lead us to assume that the result is due to an action taking place in one molecule rather than in two.

XX.—*Note on Sulphate of Alumina from Iquique, Peru.*

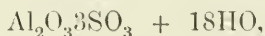
By F. FIELD, F.R.S.

(Read May 20th, 1869.)

THE following is an analysis of a fine sample of native sulphate of alumina, from Peru, after deducting small quantities of chloride of sodium, oxide of iron, and silica:—

Sulphuric acid	35.56
Alumina	15.88
Water	48.56
	<hr/>
	100.00

corresponding to the formula,



which requires

Sulphuric acid	35.93
Alumina	15.57
Water	48.50
	<hr/>
	100.00

XXI.—*On Regnault's Chlorinated Chloride of Methyl.*

By W. H. PERKIN, F.R.S.

LAST year at the British Association I gave an account of the chloride of methylene obtained from chloroform by means of nascent hydrogen. This substance I found to have a boiling point of about $40^{\circ}5$, or about ten degrees higher than that given by Regnault for the chlorinated chloride of methyl. It therefore appeared very desirable to re-examine this last-named body, and see if it really were an isomer of chloride of methylene.

To prepare the chloride of methyl for the production of this body, I found it convenient to employ purified wood spirit, saturated in the cold with hydrochloric acid gas.

This product, when heated, evolves chloride of methyl in a continuous and regular manner, and as it may be kept for a considerable time, large quantities were prepared at once.

The chloride of methyl was purified by first passing through water, and then through concentrated sulphuric acid.

In chlorinating the chloride of methyl, it was first well mixed with the chlorine gas in a small wash-bottle, before exposure to the light, and always kept in excess. The mixed gases were then passed through several lengths of quill tubing, connected together by means of vulcanized tubing, and placed outside the laboratory window so as to be thoroughly exposed to the light. The resulting chlorinated products were then passed into a wash-bottle containing water, to absorb the hydrochloric acid formed, and then absorbed by means of glacial acetic acid, which is much more convenient than condensing with ice.

This process was kept continuously at work for about a week, fresh acetic acid being used each day. The saturated acetic acid was then heated in a retort fitted with a well cooled condenser, until the temperature rose to 100° or 105° C. The distillate was mixed with water, and the heavy oil which separated was collected and dried. This oil, when heated, commenced boiling at 30° C., but the temperature rapidly rose to near 40° C., in fact the lowness of the boiling-point appeared to be entirely due to the presence of chloride of methyl dissolved in

the chlorinated bodies. About half of the product distilled between 40° and 50° , and after a few rectifications this fraction gave a product boiling between 40° and 42° , the residue being chiefly chloroform, and perhaps a little tetrachloride of carbon.

Two combustions of this product gave the following numbers:—

- I. 0.2891 of substance gave
0.1478 of CO_2 and
0.0640 of H_2O .
- II. 0.2163 of substance gave
0.1103 of CO_2 and
0.0469 of H_2O .

These numbers give percentages agreeing closely to those required by the formula



as the following comparison will show:—

		Theory.		Experiment.	
				I.	II.
C	12.0	14.12	13.94	13.90
H_2	2.0	2.35	2.45	2.40
Cl_2	71.0	83.53		
		<hr/>	<hr/>		
		85.0	100.00		

A Gay-Lussac determination of the vapour-density gave the following results:—

$$\begin{aligned}
 P' - P &= 0.1530. \\
 V &= 52.5 \text{ cc.} \\
 T &= 75^{\circ} \text{ C.} \\
 H - h &= 733 \text{ mm.} \\
 D &= 2.979. \quad \text{Theory, } 2.941.
 \end{aligned}$$

This product was therefore pure chlorinated chloride of methyl. From its boiling-point and general behaviour it appears to be identical with the chloride of methylene from chloroform. I have not, however, as yet examined its physical properties.

Chloride of methylene is not very rapidly acted upon by alcoholic hydrate of potassium, being in this particular somewhat similar to tetrachloride of carbon, but unlike chloroform,

which is quickly decomposed, yielding chloride and formate of potassium.

The President, in thanking Mr. Perkin for his communication, remarked that the experiments bore closely on a theoretical question now at issue among chemists, viz., whether atoms have bonds possessing different properties, and accordingly yielding different products as one or the other is acted upon.

Dr. Hugo Müller said that he made some experiments with the view of finding a good method of producing chloride of methylene; but he found that, at the best, it was a long and tedious operation. The best result he obtained by simply dissolving the chloroform in alcohol, and adding hydrochloric acid and zinc with a few drops of platinum chloride. The whole is warmed slightly, in order to distil off the chloride of methylene as soon as it is formed; otherwise it is further acted upon and lost. He was trying some experiments with the object of obtaining bromide of methylene from bromoform, but the difficulty of obtaining the latter in quantity prevented him from going on with the experiment. He would be glad to hear of a practicable method of obtaining bromoform.

Dr. Mills said it might be easily obtained by treating citrates with excess of bromine. He had obtained a large quantity in that way.

Dr. Müller, on the contrary, had obtained but very unsatisfactory results by this method. The yield was very small in proportion to the citric acid used.

Mr. Bassett had prepared, or attempted to prepare, bromoform in the way prescribed by Dr. Mills, but he also found that the product was very small.

Mr. Perkin mentioned that he is at present engaged in an investigation of Bunsen's gaseous bromide of methyl.

PROCEEDINGS
AT THE
MEETINGS OF THE CHEMICAL SOCIETY.
SESSION 1868-69.

November 5th, 1868.

Dr. W. A. Miller, Vice-President, in the Chair.

The following papers were read :—

“On the Hydride of Butyro-salicyl and Butyric Coumaric Acid :” by Mr. W. H. Perkin, F.R.S.

“On the Application of Chlorine Gas to the Toughening and Refining of Gold :” by F. B. Miller, F.C.S., Assayer to the Sydney Branch of the Royal Mint.

November 19th, 1868.

Extraordinary General Meeting.

Mr. Warren De la Rue, President, in the Chair.

The last four lines of the seventh bye-law were altered as follows :—

“There shall be six other Vice-Presidents who have not filled the office of President, and every year two of these Vice-Presidents shall retire from the Council, unless one of them should be nominated to the Presidency, in which case only one other Vice-President shall retire from the Council.”

The fourth, fifth, sixth, and seventh lines of the fifth bye-law are altered as follows:—

“1st. The names of the two Vice-Presidents, who it is proposed should retire from the Council, or in the case of one of them being nominated to the Presidency, from the Vice-Presidency.”

The eleventh line of the same bye-law was altered as follows:

“Names of the two new Vice-Presidents.”

The fourteenth, fifteenth, and sixteenth paragraphs of the same bye-laws were altered as follows:—

“In the event of two non-official members of the Council being nominated to the Vice-Presidency, of six new Members of Council,—or in the event of one non-official Member of Council being nominated, of five new Members.”

Ordinary Meeting.

Mr. Warren De la Rue, President, in the Chair.

The following gentleman was duly elected a Fellow of the Society:—

Dr. W. J. Palmer, Calcutta.

The following papers were read:—

“On the Action of Chloride of Lime on Aniline:” by Mr. W. H. Perkin, F.R.S.

“Analysis of a Meteorite from South Africa:” by Prof. Church.

“On the Action of Salt on Chessylite:” by Prof. Church.

December 3rd, 1868.

Mr. Warren De la Rue, President, in the Chair.

The President announced that the Council had resolved to set apart a sum of £50 as a grant fund in aid of original research.

The following gentlemen were duly elected Fellows of the Society :—

Mr. G. R. Gowland, 48, High Street, Sheffield; Mr. E. J. Tosh, Whitehaven.

Professor Wanklyn gave a verbal account of his researches on the Action of Sodium on the Ethers of the Fatty Acids.

Dr. Gladstone read a paper "On some Compounds of Phosphorus containing Nitrogen."

December 17th, 1868.

Mr. Warren de la Rue, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society :—

Mr. J. Hughes, 16, Penn Road Villas, Camden Road, Holloway; Mr. T. Rowan, North Woodside House, Glasgow; Mr. W. W. Stoddart, 9, North Street, Bristol.

The following papers were read :—

"On the Isolation of the Missing Sulphur Urea:" by J. Emerson Reynolds.

Sir Benjamin Brodie gave a short account of M. Berthelot's recent production of Hydrocyanic Acid by subjecting a mixture of Acetylene and Nitrogen to the action of a red heat.

January 21st, 1869.

Mr. Warren De la Rue, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society :—

J. F. Allen, St. Helens; E. K. Muspratt, Seaforth Hall, near Liverpool; F. W. Hart, 8, Kingsland Green; the Rev. Stephen Williams, Stonyhurst College.

The following papers were read :—

"On the Chemical Composition of Canaüba Wax:" by Nevil Story Maskelyne.

“On the Connection between the properties of Malleable Iron and Steel, and the amount of Phosphorus they contain :”
by Dr. B. H. Paul.

February 4th, 1869.

Mr. Warren De la Rue, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society :—

E. L. Barret, 44, Lawford Road, Kentish Town; J. J. Field, Highgate; W. H. Kearns, Accrington, Lancashire.

A lecture by Dr. Wallace, “On the Chemistry of Sugar Refining,” was then read by the Secretary.

February 18th, 1869.

Mr. Warren De la Rue, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society :—

Edward Duncan Holditch, 10, Bankside, Southwark; Alfred Kingsley Howard, 63, Queen's Crescent, Haverstock Hill; William Rossiter, South London College, Blackfriars Road.

Professor Wanklyn made a verbal communication “On the Hydrate of Ethylene Sodium.”

March 4th, 1869.

Mr. Warren De la Rue, President, in the Chair.

The following gentleman was duly elected a Fellow of the Society :—

J. J. Day, 53, Bedford Square.

Mr. C. Tomlinson, F.R.S., delivered a lecture “On Catharism, or the influence of Chemically Clean Surfaces.”

March 18th, 1869.

Mr. Warren De la Rue, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society :—

Thomas Bolas, 2, Little Sutton Street, Turnham Green ;
W. F. Catcheside, 53, Ackers Street, Oxford Road, Manchester ;
Frank Clowes, 15, Cornwall Place, Holloway ; Charles
Hunt, London Gas Light Company, Nine Elms.

The following papers were read :—

“On the Determination of Carbon in Cast-iron :” by
Mr. Arthur Elliott.

“On the Butylic Compounds derived from the Butyl
Alcohol of Fermentation :” by Messrs. E. T. Chapman and
Miles H. Smith.

“On a Certain Reaction of Quinine :” by Professor Stokes,
Sec. R.S.

March 30th, 1869.

Anniversary Meeting.

See pp. i to xvi.

April 1st, 1869.

Dr. Williamson, President, in the Chair.

The following gentleman was duly elected a Fellow of the
Society :—

M. Deering, Assistant Chemist to the War Department.

The following papers were read :—

“On some Decompositions of the Acids of the Acetic Series :”
by E. T. Chapman and Miles H. Smith.

“Note on Coumarin :” by W. H. Perkin, F.R.S.

April 15th, 1869.

Dr. Williamson, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

J. T. Bottomley, King's College; Frederick Braby, Mount Henley, Sydenham Hill.

The following papers were read:—

“On Propyl Compounds derived from the Propylic Alcohol of Fermentation:” by E. T. Chapman and Miles H. Smith.

“On Bromide of Amyl:” by E. T. Chapman and Miles H. Smith.

Professor Wanklyn made a verbal communication “On the Atomicity of Sodium.”

May 6th, 1869.

Dr. Williamson, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Edward Meusel, Ph.D., University Collège; John W. Muir, Shortland, Thames Gold Fields, New Zealand; A. W. Reinold, Clifton College, Bristol.

The President read a petition of the President and Council of the Chemical Society, to be presented to the Houses of Parliament, praying that such laws may be enacted as may procure for Chemistry, and other branches of Natural Science, as important a position among the studies of Endowed Schools as that now occupied by Latin and Greek.

Mr. J. Lowthian Bell delivered a lecture “On the Chemistry of the Blast Furnace.”

May 20th, 1869.

Dr. Williamson, President, in the Chair.

The following papers were read:—

“On the Constitution of Hyposulphurous Acid:” by C. Scholtemmer.

“Note on a Native Sulphate of Alumina from Peru:” by F. Field, F.R.S.

“On Regnault’s Chlorinated Chloride of Methyl:” by W. H. Perkin, F.R.S.

June 3rd, 1869.

Dr. Williamson, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

W. G. Valentine, 126, Lancaster Road, Notting Hill; T. G. Hewlett, Surgeon, Bombay Army; H. S. G. Stevenson, Oxford; Captain A. Noble, Elswick Ordnance Works, Newcastle.

Dr. Williamson gave a lecture “On the Atomic Theory:” Dr. W. A. Miller taking the Chair.

June 17th, 1869.

M. Dumas delivered the “Inaugural Faraday Lecture:” after which a vote of thanks to the Lecturer was proposed by Dr. Tyndall, and seconded by Dr. Odling.

The lecture was delivered in the Theatre of the Royal Institution.

July 1st, 1869.

Dr. Williamson, President, in the Chair.

The following papers were read:—

“Remarks on Dr. Williamson’s Address upon the Atomic Theory:” by Dr. E. J. Mills.

“On Ethyl-hyposulphurous Acid:” by Mr. R. H. Smith.

“Note on the Absorption Spectra yielded by certain Organic Substances:” by Dr. T. L. Phipson.

“Further Experiments on the Atomic Weights of Cobalt and Nickel:” by Dr. W. J. Russell.

“On the Action of Pentachloride of Phosphorus on Sulphuric Acid:” by Mr. Williams.

“Apparatus for determining the quantity of Gas dissolved in Natural Waters:” and “On a new form of Apparatus for Gas Analysis:” by Mr. Herbert McLeod.

Donations to the Library, 1868-69:—

“Catalogue of Scientific Papers (1800-1863):” compiled and published by the Royal Society of London: from the Royal Society.

“Qualitative Analysis:” by R. Fresenius: seventh edition: edited by Arthur Vacher: from the Editor.

“Water Analysis:” a practical treatise on the examination of Potable Waters: by J. A. Wanklyn and E. T. Chapman: from the Authors.

“A History of Chemical Theory from the age of Lavoisier to the present time:” by A. Wurtz: translated and edited by Henry Watts: from the Editor.

“The Elements of Heat and of Non-metallic Chemistry:” by Frederick Guthrie: from the Author.

“Lessons on Elementary Chemistry, Inorganic and Organic:” second edition: by H. E. Roscoe: from the Author.

“Systematic Technical Education for the English People:” by J. Scott Russell: from the Author.

“Notes on the Metals:” by Thomas Wood: from the Author.

“Scientific Studies:” by Henry Dircks: from the Author.

“Contribution towards a History of Electrometallurgy:” by Henry Dircks: from the Author.

“On the Crystallographic method of Grassmann:” by W. H. Miller: from the Author.

“Smithsonian Contributions to Knowledge,” vol. xv: from the Smithsonian Institution at Washington.

“The Pharmacopœia of India:” prepared by E. J. Waring, M.D.: from the Pharmacopœia of India Committee.

"The Gold-fields of Nova Scotia:" by A. Heatherington:
from the Author.

"Report of the Government Botanist and Director of the Botanic Garden at Melbourne:" by F. von Müller: from the Reporter.

"Report on Epidemic Cholera and Yellow Fever in the United States' Army during the year 1867:" from the War Department (U.S.).

"Morson and Swan's Book of Chemical Labels:" from J. C. Brough, Esq.

"On the Home Produce, Imports, and Consumption of Wheat:" by J. B. Lawes and J. H. Gilbert: from the Authors.

"On the Estimation of Potassium:" by James Chalmers and Robert Tatlock: from the Authors.

"Lecture on Perfumes, Flower-farming, and the method of obtaining the Odours of Plants:" by Septimus Piesse: from the Author.

"A Dynamical Theory of the Universe:" by James Teale:
from the Author.

"Experiments on Itacolumite:" by Charles Wetherill:
from the Author.

"Pharmacopœiæ recentiores: Anglica, Gallica, Germaniæ, Helvetica, Russiæ, inter se collatæ: scripsit H. Hager:" from the Author.

"Sur la Chaleur latente de Volatilisation du Sel-ammoniac et de quelques autres substances:" par C. Marignac: from the Author.

"Relazione alla R. Accademia delle Scienze di Torino, sulla Memoria di Giovane Struve, intitolato 'Studii sulla Mineralogia italiana: Pirite di Piemonte e dell' Elba:' da Quintino Sella:" from the Author.

"Libros del Saber de Astronomia del Rey Don Alfonso de Castilla, compilados, anotados y comentados por Don Manuel Rico y Sinobras:" from the Academy of Sciences at Madrid.

"Ueber die chemische Constitution der organischen Kohlenwasserstoffe:" von H. Kolbe: from the Author.

"Christian Friedrich Schönbein: Programm für die Rec-toratsfeier der Universität zu Basel: von Eduard Hagel-bach:" from Warren de la Rue, Esq.

The following works, from the Library of the late Robert Warington, Esq., F.R.S., have been presented to the Society by Mrs. Warington:—

"Agricolæ (Georgii) de Re Metallica, Libri xii." Folio. 1621.

"Bancroft's Experimental Researches concerning the Philo-sophy of permanent Colours." 2 vols. 8vo. 1813.

"Bergmann's Physical and Chemical Essays:" translated by Dr. Cullen. 2 vols. 8vo. 1788.

"Berthier, Traité des Essais par la Voie Sèche." 2 tomes, 8vo. 1834.

"Boyle (Hon. Robert) New Experiments, Physico-mechanical, touching the Spring of the Air and its effects, made for the most part with a new Pneumatic Engine." 4to. 1682.

———"The Sceptical Chemist." 8vo. 1680.

———"Works of, epitomized by Richard Boulton," 3 vols. 8vo. 1700.

Cavallo (Tiberius). "A complete Treatise on Electricity." 3 vols. 8vo. 1795.

Chaptal (J. A.). "Chimie appliquée aux Arts." 4 tomes. 1807.

Chevreul (E.). "Recherches sur les corps gras d'origine animale." 8vo.

Cramer (J. A.). "Elements of the Art of Assaying Metals." 8vo. 1741.

Davy, (Sir Humphry). "Researches on Nitrous Oxide." 8vo. 1800.

———"On the Safety-lamp for Coal Mines, with some researches on Flame." 8vo. 1818.

Jacquiu (J. F.). "Elements of Chemistry." 8vo. 1799 and 1803.

Hall's (Stephen) "Statical Essays concerning Hæmosta-tics." 8vo. 1740.

———"Statical Essays concerning Vegetable Statics." 8vo. 1738.

Hunt (Robert). "Researches on Light." 8vo. 1841.

- Klaproth (H. M.). "Analytical Essays towards promoting the Chemical Knowledge of Mineral Substances." 8vo. 1801.
- Lewis (William). "Course of Practical Chemistry." 8vo. 1746.
- Nauman (Caspar). "The Chemical Works of, with large additions : " by W. Lewis. 2 vols. 8vo. 1773.
- Nicholson (William). "A Dictionary of Theoretical and Practical Chemistry." 8vo. 1808.
- Orfila (M.). "Eléments de chimie, appliquée à la Médecine et aux Arts." 2 tomes 8vo. 1828.
- Parkes (Samuel). "Chemical Essays, principally relating to the Arts and Manufactures of the British Dominions : " third edition : revised by N. Hodgetts. 8vo. 1830.
- Priestley (Joseph). "Experiments and Observations on various kinds of Air." 3 vols. 8vo. 1790.
- Priestley (Joseph). "Experiments and Observations on various branches of Natural Philosophy, with a continuation of the Observations on Air." 2 vols. 8vo. 1779 and 1781.
- "Reports of the Meetings of the British Association for the Advancement of Science, from 1842 to 1864." 23 vols. 8vo.
- Rose (H.). "A Manual of Analytical Chemistry," translated from the German by John Griffin. 8vo. 1837.
- "Scheele's Chemical Essays," translated by C. Beddoes. 8vo. 1786.
- Thénard (L. J.). "The General Principles of Chemical Analysis," translated by Arnold Merriks. 8vo. 1818.
- Thomson (Thomas, M. D.). "An attempt to explain the first Principles of Chemistry." 2 vols. 8vo. 1825.
- "A system of Chemistry." 4th edition. 5 vols. 8vo. 1810.
- "A system of Chemistry of Inorganic Bodies." Seventh edition. 2 vols. 1830.
- "The Chemistry of Organic Bodies—Vegetables." 8vo. 1838.
- "The Chemistry of Animal Bodies." 8vo. 1843.
- Turner (Edward). "Elements of Chemistry." 4th edition. 8vo. 1833.
- Eighth edition, edited by Liebig and Gregory. 2 vols. 8vo. 1847.

Watt. "Correspondence of the late James Watt, on his discovery of the Theory of the Composition of Water; with a Letter from his Son:" edited, with Introductory Remarks and an Appendix, by James Patrick Muirhead. 8vo. 1846.

Watkins (Francis). "A popular Sketch of Electromagnetism and Electrodynamics." 8vo. 1828.

Periodicals:—

"Philosophical Transactions," 1868, Part I.: from the Royal Society.

"List of Officers and Fellows of the Royal Society for 1868:" from the Royal Society.

"Proceedings of the Royal Institution of Great Britain," vol. V., parts 3, 4, 5: from the Royal Institution.

"List of Members, Officers, and Professors of the Royal Institution for 1869:" from the Royal Institution.

"Quarterly Journal of Science:" from the Editor.

"Journal of the Photographic Society," from June, 1868 to May, 1869: from the Society.

"Pharmaceutical Journal and Transactions," from June, 1868 to July, 1869: from the Pharmaceutical Society.

"Journal of the Society of Arts," 1868-69: from the Society.

"Chemical News," 1868-69: from the Editor.

"The Chemist and Druggist," from July, 1868 to June, 1869: from the Editor.

"Thirty-ninth Annual Report of the Royal Cornwall Polytechnic Society," 1868: from the Society.

"Proceedings of the Philosophical Society of Glasgow," vol. IV., No. 4: 1867-68: from the Society.

"Annual Report of the Leeds Philosophical and Literary Society," for 1867-68: from the Society.

"Proceedings of the Literary and Philosophical Society of Liverpool," 1865-66 and 1866-67 : from the Society.

"Taylor's Calendar of the Meetings of Scientific Bodies," for 1868-69 : from the Publisher.

"The Canadian Pharmaceutical Journal," November, 1868 : from the Editor.

"American Journal of Science and Arts," from June, 1868 to May, 1869 : from the Editor.

"Journal of the Franklin Institute," from May, 1868 to May, 1869 : from the Institute.

"Proceedings of the American Philosophical Society," vol. X. January to March, 1867 : from the Society.

"Proceedings of the Academy of Natural Sciences at Philadelphia," 1867 : from the Academy.

"Annual Report of the Commissioner of Patents" (U.S.), for 1865 ; 2 vols. and plates : from the Commissioner.

"Cosmos," 2me série. tome VI. : from the Editor.

"Bulletin de l'Académie Royale de Belgique," 1868.

"Annuaire de l'Académie Royale de Belgique," 1869 : from the Academy.

"Académie des Sciences et Lettres de Montpellier.—Mémoires de la Section des Sciences" (1864). Tome VI. Livraison I.

"——— Extraits des Procès-verbaux des Séances," 1863—1864 : from the Academy.

"Archives Néerlandaises." Tome III., 1868 : from the Academy of Sciences at Haarlem.

"Bulletin de l'Académie Impériale de Saint Pétersbourg." Tome XII, Livraisons 3, 4, 5 ; Tome XIII, Liv. 1, 2, 3 : from the Academy.

"Giornale di Scienze naturali ed economiche, pubblicato per cura del Consiglio di Perfezionamento annesso all R. Istituto tecnico di Palermo," vol. IV., fascicoli 1, 2, 3, 4 : from the Institute.

“Berichte der deutschen Chemischen Gesellschaft zu Berlin.”
Hefte 4—12.

“Monatsberichte der Königlichen Akademie der Wissenschaften zu Berlin.” 1868, August—October: from the Academy.

“Sitzungsberichte der Königl.-bayerischen Akademie der Wissenschaften,” 1868. Band I., Hefte 2, 3, 4: from the Academy.

“Denkschriften der Kaiserlichen Akademie der Wissenschaften zu Wien.” Band XXVIII.

“Sitzungsberichte derselben.” Band LVII., Hefte 1, 2, 3: from the Academy.

“Zeitschrift für Chemie. Neue Folge.” Band VI., Hefte 11, 12; Band VII., Hefte 1—10: from the Editor.

XXII.—*Researches on the Constitution and Reactions of Tyrosine.*

By J. L. W. THUDICHUM, M.D., and J. ALFRED WANKLYN.

CONTENTS.

- Part I. Oxidation of Tyrosine by means of Bichromate of Potash and dilute Sulphuric Acid.
 Part II. Tyrosine with Mercuric and Mercurous Nitrates and Mercurous Nitrite.
 Part III. Action of Nitric and Nitrous Acids upon Tyrosine.
 Part IV. Action of Iodide of Ethyl and of Reducing agents.
 Part V. General considerations.

PART I.

Oxidation of Tyrosine by means of Bichromate of Potash and dilute Sulphuric Acid.

The behaviour of tyrosine towards bichromate of potash and dilute sulphuric acid reminded us forcibly of oxalic acid, which, as is well known, is very readily attacked by chromates in acid solution. We were unable to find any trace of acetic, benzoic, or any volatile organic acid, except formic acid, among the products of this oxidation of tyrosine. Moreover the quantity of formic acid obtained even by the most cautious oxidation was exceedingly small, as will be appreciated on considering the bearing of the following experimental details.

Took, about 3 grm. of tyrosine,
 (less than) 10 „ H_2OSO_3 ,
 100 c.c. of water,
 8 grm. of bichromate of potash.

There was violent action with evolution of carbonic acid; a slight smell of formic acid was noticed. There was formation of 3 or 4 grm. of an insoluble yellowish-green chromium-compound, of which more will be said directly. The whole product of the oxidation, including this powder, was introduced into a flask and distilled. The distillate was saturated with carbonate of baryta, and the baryta-salt resulting from this operation was weighed and found to be 0.0138 grm, which, on examination, proved to be formate of baryta. It gave off no smell of acetic or higher fatty acid on being heated with sulphuric acid. It

had the property of very easily reducing silver salts. The total quantity of formic acid obtained in the experiment was, as will be found on calculation, about $\frac{1}{500}$ of the weight of tyrosine employed. The yellowish-green chromium-compound is formed only when the proportion of sulphuric acid is small. Our analyses point to the formula $C_9H_{11}NO_{12}Cr_2O_3 \cdot 3H_2O$ as the following comparison shows:—

- I. 0.6245 gm. (dried at 105° C.) gave on combustion with chromate of lead, a little copper turnings being used, 0.200 gm. H_2O and 0.4760 gm. CO_2 . H per cent. = 3.56; C per cent. = 20.79.
- II. 0.3590 gm. gave on combustion by Dumas' process 7.99 c.c. at 0° C., and 760 mm. pressure = 0.010 gm. of nitrogen; therefore N per cent. = 2.80.
- III. 0.3820 gm. gave on cautious ignition, and subsequent moistening with nitric acid and re-ignition 0.1078 gm. of Cr_2O_3 ; therefore Cr per cent. = 19.37.

The formula $C_9H_{11}NO_{12}Cr_2O_3 \cdot 3H_2O$ requires—

	Calculated.		Found.		
			I.	II.	III.
C_9	108	20.30	20.79	—	—
H_{17}	17	3.20	3.56	—	—
N.....	14	2.63	—	2.80	—
Cr_2	105	19.74	—	—	19.37
O_{18}	288	54.13	—	—	—
	<hr/>	<hr/>			
	532	100.00			

This chromium-compound requires a good deal of drying, and the determination of the chromium presents some difficulties. It is necessary to heat very cautiously to avoid loss, and subsequently to moisten thoroughly with nitric acid and to ignite very strongly at last.

Properties of the compound $C_9H_{11}NO_{12}Cr_2O_3 \cdot 3H_2O$. It is a very light powder of a snuff colour, with a shade of yellowish-green. It is very nearly insoluble in water, insoluble in either cold or boiling acetic acid. It is slowly dissolved by hydrochloric acid. Boiling with strong hydrochloric acid occasions no evolution of chlorine, as was proved by leading the vapours into solution of iodide of potassium, from which there was no evolution of

iodine. This fact proves that the organic chromium-compound contains none of the chromium in the state of chromic acid.

Submitted to the action of heat it behaves in a very interesting manner. When a quantity of it is heated in a test-tube, long before the temperature of low redness is attained, a kind of dry effervescence sets in, the light dry powder being raised in little cones from which carbonic acid gas is very rapidly escaping. At the same time drops of water condense in the upper part of the test-tube. The residue is a pyrophorus, consisting of sesquioxide of chromium and finely divided carbon.

A quantitative determination of the products of this destructive distillation was made as follows :

0.1275 gm. was put into a narrow tube, which was subsequently drawn out so as to deliver gas, and then placed in the combustion furnace, and slowly heated to redness, the gas being collected over mercury.

The gas which was thus evolved measured 26.57 c.c. at 0° C., and 760 mm. pressure. Caustic potash was then introduced which occasioned an absorption, so as to leave a residue of 12.28 c.c. at 0° C and 760 mm. pressure.

Therefore 14.29 c.c. of CO_2 had been evolved = 0.0279 gm. of CO_2 .

The loss on heating was likewise ascertained by weighing before and after the ignition. The loss was 0.064 gm.

The total capacity of the tube was likewise measured, and found to be 5.62 c.c., and the quantity of air left in the tube at the end of the operation was measured and found to be 0.80 c.c.

Reduced to percentage we have :—

100 gm. of substance lose 50.2 gm. containing 21.9 gm. of CO_2 .

(In another experiment in which the measurements were made more roughly, 0.4905 gm. of substance experienced a total loss of 0.2445 gm. and gave off 45 c.c. of CO_2 .)

If the difference between the total loss and the CO_2 be taken as water, we have :—

100 gm. of substance lose
28.3 gm. water,
21.9 gm. CO_2 .

As no oxidising agent was used in this experiment, it follows that the oxygen evolved in the form of carbonic acid

and water was oxygen originally contained in the substance.

28.3 grms. of water contain 25.2 grms. of oxygen.

21.9 grms. of CO_2 contain. . 15.9 grms. of oxygen.

41.1

The experiment has therefore shown that, exclusive of the oxygen remaining in combination with the chromium, there is 41.1 per cent. of oxygen in the original compound. The theoretical percentage of oxygen uncombined with the chromium in the original compound is 45.1, as may be found on reference to the analysis. For a direct determination of oxygen the approximation is sufficiently close.

Another interesting consequence deducible from the experiment is that one-third of the total carbon of the substance escapes as carbonic acid, and two-thirds of the total carbon remain along with the sesquioxide of chromium, constituting the pyrophorus.

A considerable quantity of $\text{C}_9\text{H}_{11}\text{NO}_{12}\text{Cr}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ has been prepared on different occasions. An attempt was made to get a base from it by reduction with hydriodic acid. The following are the details:—

3.50 grm. of $\text{C}_9\text{H}_{11}\text{NO}_{12}\text{Cr}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and 35 c.c. of hydriodic acid of sp. gr. 1.67 at 20°C ., and a little phosphorus, was boiled until half of the acid had distilled over. There was some reduction evidenced by liberation of iodine. The residue was diluted with water, supersaturated with potash, and distilled. In the distillate no base except ammonia was found, and there was only a trace of ammonia, as was shown by the following:—The distillate, after being rendered acid by hydrochloric acid was subsequently concentrated by evaporation in the water-bath, and then precipitated by chloride of platinum. The total quantity of chloroplatinate weighed 0.0786 grm., which on further drying weighed 0.0782 grm., and contained 0.0342 grm. of platinum or 43.74 per cent. (Chloroplatinate of ammonium yields 44.3 per cent. of platinum.)

Most probably this trace of ammonia is purely accidental, and at any rate it is not a main product. Hydriodic acid, therefore, does not reduce the chromium-compound so as to form a base.

Finally, the *yield* of the compound and the conditions under

which it is formed, were studied, and also the quantity of oxygen consumed in its production.

From 100 parts of tyrosine it is easy to obtain quite 100 parts of the chromium-compound. As before mentioned, excess of sulphuric acid must be avoided in the preparation of the substance. The following experiments illustrate the necessity of attending to this particular:—

Took 1.195 gm. of tyrosine, and dissolved it in hot water. Then added 10 gm. of bichromate of potash, which, along with 11 gm. of H_2OSO_3 , had been previously dissolved in 100 c.c. of water. There was reaction, but *no* formation of the insoluble chromium-compound.

Took 1.00 gm. of tyrosine,
3.00 gm. $\text{K}_2\text{O}_2\text{CrO}_3$,
1.00 c.c. H_2OSO_3 .

The bichromate of potash was dissolved in 50 c.c. of water, to which the sulphuric acid was added, and finally the tyrosine was added. It dissolved completely, and, on boiling, a precipitate of the chromium-compound was obtained, which, when washed and dried, weighed 1.108 gm.

On making a calculation of the amount of chromium-compound which a given weight of tyrosine could give, supposing total conversion into the chromium-compound, it will be seen that not so much as half the tyrosine is converted in the actual case.

The liquid which deposits the chromium-compound no doubt contains the remainder of the tyrosine, either as such, or in combination with sulphuric acid.

We have, moreover, observed that after the deposit of so much chromium-compound as is readily formed, a further crop of it may be obtained by long-continued boiling of the filtrate.

An estimation of the quantity of oxygen consumed in forming a given quantity of chromium-compound was effected as follows:—

A standard solution of bichromate of potash was made, containing 49.2 milligrammes of bichromate in every cubic centimetre. Each c.c. therefore contained 8 milligrm. of active oxygen.

A solution of protochloride of tin in hydrochloric acid was made of such a strength that *one measure* (5 c.c.) took 4.6 c.c. of

the standard bichromic solution to oxidize it completely. (Iodide of potassium and starch employed.)

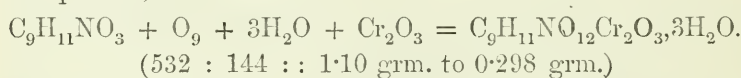
Took 1.00 grm. of tyrosine,

0.5 c.c. of H_2OSO_3 ,

50 c.c. of standard bichromate solution. Boiled: a precipitate formed. Filtered, and made up the filtrate to 100 c.c. Then titrated the filtrate. Found that one measure (5 c.c.) of the protochloride of tin took 21.5 c.c. of this filtrate. The whole filtrate, therefore, contained $21.4 \times 8 = 171.2$ milligrm. of active oxygen.

There were employed $50 \times 8 = 400$ milligrm. of active oxygen.

Therefore, $400 - 171.2 = 228.8$ milligrm. of oxygen had been consumed by one grm. of tyrosine in giving the insoluble chromium-compound. From the 1.00 grm. of tyrosine the yield is, as determined by other experiments, 1.10 grm. of chromium-compound. If a calculation be made, it will be found that 0.298 grm. of oxygen is required to oxidize tyrosine according to the equation,



The quantity of oxygen consumed in making 1.10 grm. of $\text{C}_9\text{H}_{11}\text{NO}_{12}\text{Cr}_2\text{O}_3, 3\text{H}_2\text{O}$ is calculated to be 0.298 grm., and found to be 0.229 grm. The difference is probably due to our having rated the yield a little too high. A yield of 1.0 grm. of chromium-compound would require 0.270 grm. of oxygen. In either case it is quite plain that no other oxidation had taken place, and that the tyrosine which had not become $\text{C}_9\text{H}_{11}\text{NO}_{12}\text{Cr}_2\text{O}_3, 3\text{H}_2\text{O}$ remained unoxidized in the solution.

When tyrosine, therefore, is boiled with a solution of bichromate of potash, and not more than twice as much sulphuric acid as tyrosine, it is partially resolved into a singular chromium-compound, and the rest of it remains unoxidized.

When excess of acid is taken, so as to avoid formation of the insoluble chromium-compound, there is oxidation down to carbonic acid and water; a little formic, but no other volatile acid being produced.

The following experiment illustrates this fact:—

Took 1.00 grm. tyrosine,
3.25 grm. $\text{K}_2\text{O}_2\text{CrO}_3$,
3.00 c.c. H_2OSO_3 ,

and water up to 20 c.c. Great evolution of carbonic acid took place. After having kept the product at ordinary temperatures for some weeks, we distilled it, and converted the distillate into a baryta-salt. Weight of baryta-salt, 0.080 gm., which consisted *only* of *formate* (a little of it reduced nitrate of silver very readily and abundantly and no smell of acetic or other acid could be observed on warming with H_2OSO_3).

In this experiment, therefore, about 3 per cent. of formic acid had been given by the tyrosine. Neither much nor little sulphuric acid enables bichromate of potash to convert tyrosine into any other volatile acids except carbonic and formic.

This result is in contradiction to Fröhde, according to whom acetic and other acids are produced, and negatives the theories brought forward respecting the rational formula of tyrosine, which represent it as containing the radical ethyl.

PART II.

Tyrosine with Mercuric and Mercurous Nitrates and Mercurous Nitrite.

It is known that a deep red precipitate is obtained when tyrosine is boiled with these mercurial compounds. We have made a study of the tyrosine-compound produced by this means.

One gramme of tyrosine was dissolved in about 300 c.c. of boiling water, and mercuric and mercurous nitrates added, when a pale pinkish precipitate formed. This precipitate rapidly became crimson. The mercurous nitrate which was used contained some nitrite.

The precipitate was collected on a filter, washed and dried, first at 100°C ., and ultimately at 110°C . After being detached from the filter, it weighed 2.85 grammes. It was still further dried and analysed, with the following results:—

- I. 0.6870 gm., burnt with chromate of lead and a little copper turnings, gave 0.087 gm. H_2O , and 0.405 gm. of CO_2 .
Therefore, H per cent. = 1.41, and C per cent. = 16.08.
- II. 0.7125 gm., burnt with oxide of copper and copper turnings, gave 33.33 c.c. of nitrogen gas at 0°C ., and 760 mm.
= 0.04186 gm. Therefore, N per cent. = 5.87.
- III. 0.460 gm., ignited with chromate of lead and copper

turnings, gave 0.276 grm. of mercury. Therefore, Hg per cent. = 60.00.

These results accord with the formula $C_9H_9(NO_2)_2NO_3Hg_2$.

	Calculated.		Found.		
			I.	II.	III.
C ₉	108	16.00	16.08	—	—
H ₉	9	1.34	1.41	—	—
N ₃	42	6.26	—	5.87	—
Hg ₂	400	59.61	—	—	60.00
O ₇	112	16.69	—	—	—
	<hr/>	<hr/>			
	671	100.00			

The following particulars relative to the production of the compound were ascertained. In two experiments the yields were respectively 318 and 320 from 100 parts of tyrosine. The theoretical yield for the total conversion of tyrosine into the mercury-compound $C_9H_9(NO_2)_2NO_3Hg_2$, is 370.7 parts of mercury-compound from 100 parts of tyrosine. From this it would seem that there is some slight destruction of the tyrosine during the process. Still, as the loss is only about 14 per cent., the destruction cannot be great.

The following details of an experiment may be cited:—Took 0.50 grm. of tyrosine and dissolved it in 300 c.c. of boiling water. Then added 15 c.c. of mercuric nitrate (strength: Liebig's standard for the determination of urea). There was no precipitation, only a red coloration. Added 10.5 c.c. of mercurous nitrate and nitrite (strength: 2.60 grm. of mercury in the 10.5 c.c.). Immediately on the addition of the mercurous salt the red precipitate fell down. This precipitate was put on a filter, washed and dried, and detached from the filter.

Ultimately it was dried at 110° C.

Weight of red precipitate (detached from filter) = 1.50 grm.

Weight adherent to filter = 0.10 „

Total = 1.60 „

The amount adherent to the filter was determined by combustion of the paper and estimation of the mercury, from which the quantity adherent to the paper admits of calculation.

Therefore, 100 parts of tyrosine yield 320 parts of the red compound.

The filtrate from the red precipitate was tested for mercuric salts by means of caustic alkali. There was no precipitation of mercuric oxide. In a second experiment, which differed from the first only in there being only 100 c.c. of boiling water instead of 300 c.c., absence of mercuric salts in the filtrate was likewise observed.

The mercurous salt, on the other hand, takes no direct part in the reaction. A quantitative determination has shown that as much is to be found after the reaction as was originally added.

The function of the mercurous salt is simply to convey nitrous acid or possibly simply to convey oxide of nitrogen (NO).

This is shown by the following facts:—

As a preliminary, it was proved that the mercurous salt contained some nitrite, by making an experiment in which all the mercurous compound was precipitated by chloride of sodium, filtering, and testing the filtrate (which would then contain any nitrite in the form of soda-salt) with permanganate solution. A great deal of permanganate was decolorised, showing the presence of nitrite in the original solution.

It was next shown that, although all the mercurous compound remains intact during the production of the red precipitate, nevertheless a large quantity of mercurous compound must be added in order to get the full yield of red compound. Thus 0.50 gm. of tyrosine and 15 c.c. of mercuric nitrate and only 2 c.c. of mercurous salt yielded only 1.08 gm. of red compound: whilst 0.50 gm. tyrosine, 15 c.c. mercuric nitrate, and 10.5 c.c. mercurous salt yielded 1.60 gm. of red compound.

When the mercurous salt is not added at all, and when double the quantity of mercuric salt is used, a pale pink precipitate is formed, which weighs still less.

Took 0.50 gm. tyrosine and
30 c.c. of mercuric nitrate.

The yield was 0.96 gm., and moreover the precipitate was quite different from the crimson compound. Finally, if tyrosine and mercuric nitrate, free from mercurous salt, be boiled, and oxide of nitrogen passed into the boiling liquid, immediately on the contact of the gas with the liquid, the dark red precipitate

will begin to form and a tolerable yield of the red compound may be obtained.

The formula for the red compound $C_9H_9(NO_2)_2NO_3Hg_2$ (more logically we should have written $C_9H_9N_3O_7Hg_2$) is to be taken quite empirically.

The red compound is attacked by alkalies with considerable energy, either potash or ammonia forming a deep-coloured red solution which deposits a sepia-like precipitate.

Nitric acid dissolves the red compound, forming a red solution, which evolves gas on being warmed.

PART III.

Action of Nitric Acid upon Tyrosine.

According to Strecker the first action of nitric acid on tyrosine consists in the formation of nitrate of nitrotyrosine, which crystallises very beautifully. According to Städeler,* when the treatment with the acid is pushed further a dinitro-compound is formed.

Städeler's investigation of this product does not, however, include a determination of the proportion of nitrogen in it, and, therefore, does not exclude the possibility of there being O_3 in place of NO_2 in the formula of his compound.

Thus, in his so-called dinitrotyrosine, Städeler found 39.30 per cent. of carbon and 3.46 per cent. of hydrogen; the nitrogen was not estimated.

This agrees with the formula $C_9H_{10}(NO_2)NO_6$ quite as well as with $C_9H_9(NO_2)_2NO_3$, as the following comparison shows:—

Calculated.						Found.
$C_9H_{10}(NO_2)NO_6$.			$C_9H_9(NO_2)_2O_3$.			
C_9	108	39.42	C_9	108	39.85	39.30
H_{10}	10	3.65	H_9	9	3.32	3.46
N_2	28	—	N_3	42	—	
O_8	128	—	O_7	112	—	
	<hr/>	<hr/>		<hr/>	<hr/>	
	274	100.00		271	100.00	

In like manner the analyses of the salts of so-called dinitrotyrosine accord with either formula; thus in dinitrotyrosine-line

* *Ann. der Chem. u. Pharm.* (1860) vol. cxvi, p. 82.

Städeler found 15·07 per cent. of CaO , and wrote the formula $\text{C}_9\text{H}_7(\text{NO}_2)_2\text{NO}_3\cdot\text{CaO}\cdot 3\text{H}_2\text{O}$, whilst the formula $\text{C}_9\text{H}_8(\text{NO}_2)\text{NO}_6\cdot\text{CaO}\cdot 3\text{H}_2\text{O}$ will do equally well.

$\text{C}_9\text{H}_8(\text{NO}_2)\text{NO}_6\cdot\text{CaO}\cdot 3\text{H}_2\text{O}$ requires CaO per cent. = 15·30.

$\text{C}_9\text{H}_7(\text{NO}_2)_2\text{NO}_3\cdot\text{CaO}\cdot 3\text{H}_2\text{O}$ requires CaO per cent. = 15·43.

There was found CaO per cent. = 15·07.

We have hitherto failed in the attempt to make dinitrotyrosine, but have, on the other hand, succeeded in obtaining evidence of the existence of such a product as nitro-tyrosic acid, viz., $\text{C}_9\text{H}_{10}(\text{NO}_2)\text{NO}_6$, or at any rate the corresponding lime-salt.

4 gram. of tyrosine was converted into nitrate of nitrotyrosine thus:—It was made into a paste with 16 gram. of water, and to this paste 16 gram. of nitric acid, sp. gr. 1·3, was added by degrees. The tyrosine dissolved, the solution becoming hot and assuming a yellow and then an orange colour, but evolving only traces of gas. At this stage the vessel containing the materials was immersed in cold water, whereupon an abundant crop of crystals formed so as to make a magma, which was got on to a filter, and after having been drained from the mother-liquor, dried by pressure between folds of bibulous paper. The solid citron-yellow cake of nitrate of nitrotyrosine thus obtained was mixed with 16 grms. of water and 16 grms. of nitric acid (sp. gr. 1·3), according to Städeler's prescription, and subsequently evaporated at a very gentle heat (in a sand-bath gently heated by steam).

During this operation there was first frothing; later a perfect solution was given, which was dark green at first and afterwards became red. The yellow residue was resinous whilst hot, but became brittle on cooling. It dissolved in water without difficulty, and the solution so resulting was filtered from some resinous matter and boiled with excess of carbonate of lime. In this way a deep red solution of a lime-salt was obtained which, on standing over night, deposited a small crop of very beautiful orange-yellow crystals having a singular bronze lustre, and consisting of plates of irregular shape.

This crop of crystals was dried by standing over sulphuric acid, and weighed only 0·160 gram. A very careful determination of nitrogen was made in 0·0663 gram. of the crystals by

combustion with oxide of copper and copper turnings, the gas being collected and measured over mercury.

Vol. of N + NO = 4.9 c.c. at 18° C. (dry) and 704.4 mm. pressure, or 4.26 c.c. at 0° C. and 760 mm. pressure.

Vol. of N (after removal of the NO by means of excess of oxygen and pyrogallate of potash) = 2.6 c.c. at 18° C. and 704.4 mm. (dry), or 2.27 c.c. at 0° C. and 760 mm. pressure.

Therefore total nitrogen gas equals 3.27 c.c. at 0° C., and 760 mm. = 0.00408 gram. of nitrogen, or N per cent. = 6.08.

A determination of calcium was also made in 0.0943 gram. by ignition with H_2OSO_3 , whereby 0.0335 gram. of CaOSO_3 was obtained; therefore Ca per cent. = 10.45.

These determinations accord sufficiently with the formula of an oxidized nitro-salt of calcium, viz., with $\text{C}_9\text{H}_5\text{Ca}(\text{NO}_2)\text{NO}_6 \cdot 3\text{H}_2\text{O}$ which requires:—

	Calculated.		Found.	
			I.	II.
C ₉	108	29.51	—	—
H ₁₄	14	3.82	—	—
N ₂	28	7.65	6.08	—
Ca.....	40	10.93	—	10.45
O ₁₁	176	48.09	—	—
	<hr/>	<hr/>		
	366	100.00		

Städeler's formula for dinitrotyrosate of calcium requires 11.5 per cent. of nitrogen, which does not agree with our analysis.

The circumstance that, as just described, there is evolution of gas, and green coloration of the liquid (evidently from N_2O_3) even on very careful treatment of nitrotyrosine with dilute nitric acid, is in itself a strong indication that the action of the nitric acid on nitrotyrosine consists of an oxidation (a mere substitution of NO_2 for H gives rise to water as the complementary product).

There can be very little doubt that Städeler's dinitrotyrosine was an oxidized nitrotyrosine.

When the action of nitric acid is pushed further, there is, as others have observed before us, an abundant production of oxalic acid. From 4 gramm. of tyrosine we obtained 0.6435 gramm. of perfectly dry pure oxalate of ammonia, and we think it probable that about an equal quantity was lost in the washing, so that the yield of oxalic acid by oxidation of tyrosine with nitric acid is very considerable.

A combustion of 0.1550 gramm. of this ammonia-salt with oxide of copper and copper turnings, gave 0.0990 gramm. H_2O and 0.091 gramm. CO_2 .

$\text{C}_2\text{O}_4(\text{NH}_4)_2\text{H}_2\text{O}$ requires—			Found.
C_2	24	16.90	16.01
H_{10}	10	7.04	7.10
N_2	28	—	—
O_5	80	—	—
	<hr/> 142	<hr/> 100.00	

From the ammonia-salt we made a silver-salt, which was analysed as follows:—

I. 0.3045 gramm., dried in vacuo over H_2SO_3 , was burnt with oxide of copper, and gave 0.0089 gramm. H_2O , and 0.0862 gramm. CO_2 .

II. 0.6195 gramm. of silver-salt dried at 80°C ., gave on combustion with oxide of copper, 0.0085 gramm. H_2O , and 0.1760 gramm. CO_2 . These numbers accord with the formula of oxalate of silver.

Calculated.		Found.	
		I.	II.
C_2	24 7.89	7.74	7.75
H_0	0 0.00	0.29	0.15
Ag_2	216 71.05	—	—
O_4	64 21.06	—	—
	<hr/> 304 100.00		

The explosive character of the silver-salt on being heated, also the insolubility of the lime-salt in acetic acid, and the production of carbonic oxide on strongly heating the lime-salt, were verified. The analysis of the silver-salt shows that no mes-oxalic acid is produced, a circumstance to which we attach some importance. There is moreover no production of picric acid.

Action of Nitrous Acid.

According to Studeler, nitrous acid also produces dinitro-tyrosine. We have not been able to verify this observation. When tyrosine is suspended in water through which N_2O_3 (evolved by the action of nitric acid on arsenious acid) is passed, gradual solution of the tyrosine takes place, the liquid assuming a yellow colour and evolving some gas. This solution was saturated with carbonate of lime, filtered, and the filtrate left to evaporate over sulphuric acid. A brown scum continually formed on the surface of the solution of lime-salt; this was removed by filtration, and acetate of lead was added to the filtrate, wherein it occasioned a chocolate-coloured precipitate of lead-salt. This precipitate was washed, dried at $110^\circ C.$, and analysed.

- I. 0.4660 grm. burnt with oxide of copper and a little copper turnings gave 0.0840 grm. of H_2O and 0.3880 grm. of CO_2 ; therefore C per cent. = 22.71 and H per cent. = 2.00.
 II. 0.1755 grm. gave 6.42 c.c. nitrogen at $0^\circ C.$, and 760 mm. = 0.00807 grm. N per cent. = 4.60.
 III. 0.2600 grm. ignited with H_2OSO_3 gave 0.1970 grm. of $PbOSO_3$. Pb per cent. = 51.77.
 IV. 0.1425 grm. gave 0.105 grm. $PbOSO_3$; therefore Pb per cent. = 50.34.

	Calculated.		Found.			
			I.	II.	III.	IV.
C_8	96	23.71	22.71	—	—	—
H_7	7	1.73	2.00	—	—	—
N.....	14	3.46	—	4.60	—	—
Pb.....	207	51.23	—	—	51.77	50.34
O_5	80	19.87	—	—	—	—
	<hr/>	<hr/>				
	404	100.00				

It would, therefore, seem that nitrous acid disintegrates the tyrosine to a certain extent, at any rate under the influence of an alkali.

The acid corresponding to this lead-salt should have the formula $C_8H_9NO_5$, and be derived from tyrosine as follows:—



Inasmuch as the new compound is highly coloured, analogy would lead us to suspect that it is derived from tyrosine by condensation of the molecule ; probably, therefore, the formula is at least double.

PART IV.

Action of Iodide of Ethyl.

We sealed up together 1.00 gm. of tyrosine with about 4 gm. of iodide of ethyl and heated the mixture to 100° C. The tyrosine shrunk together in a wonderful manner, but on subsequently opening the tube and warming at 100°, all the iodide of ethyl evaporated, leaving the one gramme of tyrosine unaltered in weight, and apparently quite unchanged in properties. There is, therefore, no easy action between tyrosine and iodide of ethyl.

Action of Reducing Agents.

We failed to reduce tyrosine by means of hydriodic acid at 130° C.

PART V.

General Considerations.

The chemical history of tyrosine is now sufficiently complete for the determination of its rational constitution.

The nitrogen contained in it cannot be in the nitro-state, because Will and Varrentrappe's process is available for the estimation of the nitrogen. Neither can the nitrogen exist as amidogen or as imidogen. Iodide of ethyl effects no substitution. Therefore, the nitrogen must be altogether in direct combination with the carbon.

There is no hydroxyl, otherwise hydriodic acid would effect a reduction. Therefore, all the oxygen must be in direct and complete union with the carbon. There is certainly no sign of highly condensed oxygen in tyrosine.

Tyrosine appears to be derived from C_9H_{20} , being the fully expanded hydride of nonyl, which has undergone substitution to a considerable extent, three atoms of hydrogen having been replaced by N''' and six atoms of hydrogen by three atoms of oxygen.

Tyrosine ought to be volatile, without decomposition, at diminished barometric pressure. At one pole of the molecule there will exist N''' , at the other pole $CO \cdot H$, thus:—



The great stability of tyrosine is a sign that the grouping of its carbon is regular. Everything in its chemical history converges towards this rational formula.

The fact that with dilute chromic acid it gives no acetic acid negatives the assumption of there being ethyl in union with part of the nitrogen, or in union with oxygen. The easy formation of carbonic acid is in harmony with the existence of the three atoms of carbonic oxide. The non-production of picric acid by oxidation with nitric acid is significant of the non-existence of the aromatic group.

The remarkable chromium-compound is most probably a compound highly charged with hydroxyl, thus:—



The hydrated oxide of chromium being possibly tacked on to the nitrogen, which has the faculty of being pent-atomic; and the salts of tyrosine in general are probably held together by the pent-atomic power of the nitrogen.

(The researches described in this paper have been made in the pathological laboratory at St. Thomas's Hospital).

Pathological Laboratory, St. Thomas's Hospital;
July, 1869.

XXIII.—*Note on Oxalate of Silver.*

By J. L. W. THUDICHUM and J. ALFRED WANKLYN.

IN Gmelin's Handbook (see Watts's Translation) the statement occurs that oxalate of silver retains most obstinately 2 per cent. of water, and the impression is conveyed that this compound cannot be obtained in a state of dryness.

Having recently had occasion to prepare some oxalate of

silver, we have examined this question, and have arrived at the conclusion that there is no particular difficulty in drying oxalate of silver.

The salt was obtained by double decomposition of nitrate of silver and oxalate of ammonia. It was well washed and dried over sulphuric acid in vacuo; and ultimately at 110° C. (We do not think that the drying at 110° C. was absolutely necessary).

I. 0.9087 grm. burnt with oxide of copper (without extra oxygen in the free state) gave 0.0085 grm. H_2O and 0.2565 grm. of CO_2 . H per cent. = 0.10; C per cent. = 7.70.

II. 1.6636 grm. was dissolved in nitric acid, and precipitated by means of hydrochloric acid, and gave 1.5675 grm. of chloride of silver. Ag per cent. = 70.92.

Oxalate of silver requires:

	Calculated.		Found.	
			I.	II.
C_2	24	7.89	7.70	—
Ag_2	216	71.05	—	70.92
O_4	64	21.06	—	—
	<hr/>	<hr/>		
	304	100.00		

From which we see that the silver falls only 0.13 per cent. below the calculated proportion, and that consequently there could not be more than 0.2 per cent. of water left in the oxalate of silver.

XXIV.—*Note on Dumas's Method of Determining Nitrogen.*

By J. L. W. THUDICHUM and J. ALFRED WANKLYN.

HAVING recently had considerable experience in determinations of nitrogen, we think it may possibly be of service to place on record the following laboratory-notes.

(1.) The employment of the air-pump, as Maxwell Simpson has shown long ago, may be entirely dispensed with. There is no difficulty in driving out the air so perfectly by means of the stream of carbonic acid gas alone, that 50 cub. cents. of the escaping carbonic acid shall not contain more than $\frac{1}{100}$ c.c. of air.

(2.) A good mixture for generating carbonic acid consists of bichromate of potash and carbonate of soda. The salts (separately) should be dried strongly (fused, if convenient), powdered, and then mixed. The proportions do not matter much. A very small bulk of the mixture goes a great way, giving off much gas. The advantage of being in this way able to have the carbonic acid dry is obvious.

(3.) As a practical fact, there is always, or nearly always, a little binoxide of nitrogen formed in these nitrogen determinations, and, where it is least expected, often a great deal. The plan recommended by Frankland for dealing with this gas has answered admirably in our hands. It consists, as is well known, in reading the volume of the original gas, then passing up a slight excess of oxygen (which combines with the nitric oxide) and finally absorbing the excess of oxygen by means of pyrogallate of potash, and reading again. The mean is the true volume of nitrogen. We may just warn experimenters against measuring nitrogen gas (from a Dumas's determination) over water. The trace of oxygen dissolved in water is a source of inaccuracy, and becomes appreciable in operations involving large volumes of water. Measurement over mercury should always be resorted to in these cases.

XXV.—*Further Experiments on the Atomic Weight of Cobalt and Nickel.*

By W. J. RUSSELL, Ph.D.

(Read July 1st, 1869.)

IN 1863 I described in this Journal* some experiments on the atomic weight of cobalt and nickel. The special point in these determinations was that they were made by a very simple and direct process, perhaps more simple than any which had been before used for this purpose, namely, by the reduction of the oxide with hydrogen, a process which, when applicable, has generally been preferred by chemists to all others. It is well known that this method had not previously been applied to these metals, simply because it was supposed that the oxides

* Vol. xvi. (N.S., vol. i.), p. 51.

could not be obtained of sufficiently definite composition. I showed, however, that any oxide of cobalt heated strongly over a blast lamp out of contact with the air, became changed into a light brown powder of definite composition, and further that when boiled with hydrochloric acid it gave off no free chlorine. Again, it was also proved that if any oxide of nickel be very strongly heated for some length of time over a blast lamp, it also gives an oxide of definite composition, and one which appears to be the mon-oxide. It has a green colour and differs from the cobalt-oxide in exhibiting no tendency to absorb oxygen from the air, so that it may be prepared by heating the oxide of nickel either in an atmosphere of carbonic acid or of air. With regard to the purification which the metals underwent before being used in the determinations, the process is described in full in the paper referred to, and it is shown that all the impurities capable of being removed by the process were so removed, for on repeating the process a second, and even a third time, no alteration was made in the composition of the oxide.

Since my experiments were made, two other chemists, namely, Sommaruga and Winkler, have experimented on this subject, and with very different results; the former obtained for cobalt the atomic weight 29·99 by reducing the roseo-cobaltic chloride with hydrogen, and 29·01 for nickel, by estimating the amount of sulphuric acid in the double nickel and potassic sulphate. Winkler, on the other hand, obtained 29·49 for cobalt and 29·53 for nickel, by reducing a neutral solution of the sodium-gold chloride with metallic cobalt and nickel, and weighing the gold precipitated. Using for the moment the old atomic weights for the sake of comparison, the following is a list of the numbers which the different experimenters have obtained, commencing with the highest atomic weights:

Cobalt.		Nickel.	
Schneider	30·01	Rothoff	29·53
Sommaruga	29·99	Winkler.....	29·53
Dumas	29·54	Dumas	29·51
Gibbs.....	29·50	Russell	29·37
Winkler.....	29·49	Marignac	29·35
Rothoff	29·47	Erdmann	29·10
Marignac .. { (1)	29·46	Schneider	29·03
{ (2)	29·39	Sommaruga ..	29·01
Russell	29·37		

Of the two numbers obtained by Marignac the highest was deduced from experiments on the chloride, the lowest by experiments on the sulphate of cobalt.

As a general result, it appears that when similar salts of the two metals have been used for the determinations by the same experimenter, he has obtained very nearly similar atomic weights for both metals, and in most cases a number which differs very appreciably from the atomic weights as determined by other experimenters.

In 1867 Dr. R. Schneider communicated a paper to "Poggendorff's Annalen," expressing his high appreciation of Sommaruga's determination of the atomic weight of these two metals,* and calling attention to the fact that they coincide almost exactly with the numbers which he had previously obtained; he also tries to explain why the numbers which I had obtained differ so much from his and Sommaruga's numbers. His views, which were unsupported by experiments, were that, as my number for cobalt was so much lower than his, I must in the cooling down of my cobalt have let in air, and thus obtained some oxide. On the other hand, my number for nickel was higher than his, and this is accounted for on the supposition that some oxide higher than the monoxide always escaped decomposition. From collateral evidence neither of these theories appeared at all probable, and from what follows it will be seen that they are entirely without foundation.

In a paper† communicated to this Journal last year, I showed that small quantities of a gas given off in a reaction might be measured with very considerable accuracy, and at the expense of very little time and trouble. It naturally occurred to me that it would be interesting to use the same cobalt and nickel experimented with before, and determine the atomic weights from the volume of hydrogen evolved, when a known weight of the metal was dissolved in hydrochloric acid. The form of apparatus used to collect and measure the hydrogen was precisely similar to that described in the paper above alluded to, and in the same way the weight of the gas was deduced from its volume. Some experiments with zinc and magnesium given in the paper show the degree of accuracy obtainable by this method. One or two other experiments made since then may also be quoted.

* Poggendorff's Annalen, vol cxxx., p. 303.

† Journ. Chem. Soc., vol. xxi. (N.S., vol. vi.) p. 310.

In all these experiments only very small quantities were used, hardly ever more than 0·2 grm.; with larger quantities of course the method would be proportionally more accurate. A specimen of zinc gave the following results in three consecutive experiments:—

	Vol. of hydrogen.	Weight of hydrogen from 100 pts. of zinc.
0·1855 grm. gave	281·07	3·053
0·1840 ,,	278·57	3·051
0·1883 ,,	285·01	3·050

The metal was in each case dissolved in 3 c.c. of a mixture of two parts of hydrochloric acid sp. gr. 1·155, and one part of water. Taking 65 as the atomic weight of zinc, 100 parts ought to give 3·077 parts of hydrogen. The amount of zinc in this specimen is thus from these three experiments 99·22, 99·16, and 99·13.

A specimen of pure iron wire given me by Dr. Matthiessen, when dissolved in hydrochloric acid gave the following results :

Weight of iron taken.	Vol. of hydrogen.	Weight of hydrogen from 100 pts. of iron.
0·1776	314·43	3·571
0·1781	315·06	3·569

Taking the atomic weight as 56, 100 parts should yield 3·571 per cent. of hydrogen. In all these experiments the logarithm of the weight of one volume of hydrogen is $\bar{5}·3047564$.

On examining the cobalt which had been used in the former experiments, the metal was generally found to have become covered with a brown oxide. A portion of this metal, about the quantity required for an experiment, was cut off and placed in a platinum crucible, and a stream of pure dry hydrogen was passed through the crucible as in the former experiments. After the air had been thoroughly expelled, the crucible was strongly heated for 10 to 15 minutes over a blast lamp, and then allowed to cool gradually in an atmosphere of hydrogen. If it happened that the hydrogen continued to burn as it came in contact with the air, owing to the action of the platinum, the whole crucible was surrounded with an atmosphere of carbonic acid ; this was easily done without stopping the current of hydrogen, by placing a large vessel with marble and hydrochloric acid under the

crucible as it stood on the retort stand, and a cap of paper over the crucible; in this way the platinum soon cooled down and the burning ceased.

In the following experiments both the cobalt and nickel were dissolved in 3 c.c. of a mixture of two parts of hydrochloric acid of 1.155 sp. gr. and one part of water.

Dilute sulphuric acid was tried, but it acted but slowly on the metals.

The metallic nickel appears to have undergone no change by contact with the air, for in the succeeding experiments it will be seen that identical results are obtained with nickel just as it remains from the former experiments, and the same metal again heated in hydrogen. The metal had been kept in small stoppered bottles.

Specimen No. 1. 1st Purification.

No. of experiment.	Weight of cobalt taken.	Vol. of hydrogen.	Weight of hydrogen from 100 pts. of cobalt.
1	0.1958	321.36	3.395
2	0.1905	312.95	3.398
3	0.1946	319.63	3.397
4	0.2002	328.96	3.398
Mean ..			3.397

This specimen of cobalt in the former experiments, when the oxide was reduced, gave numbers which would lead to the atomic weight 29.36. These experiments give the number 29.43. In experiments No. 2 and No. 4 the metallic cobalt was obtained by reducing some oxide which had not been used in the former experiments. Experiments No. 1 and No. 3 were made on the metallic cobalt obtained in the former experiments. In all these experiments the logarithm of the weight of one volume of hydrogen was $\bar{5}.3156213$.

Specimen No. 1. 2nd Purification.

No. of experiment.	Weight of cobalt taken	Vol. of hydrogen.	Weight of hydrogen from 100 pts. of cobalt.
1	0.1996	328.43	3.403
2	0.200	329.55	3.401
3	0.1721	290.17	3.401
Mean ..			3.402

The former experiments with this specimen of cobalt gave the atomic weight 29·37; these experiments give 29·39. Experiment No. 3 was purposely made after the whole apparatus had been taken to pieces, removed to another laboratory, and a fresh portion of air introduced into the pressure-tube.

Specimen No. 1. 3rd Purification.

No. of experiment.	Weight of cobalt taken.	Vol. of hydrogen.	Weight of hydrogen from 100 pts. of cobalt.
1	0·1877	308·97	3·404
2	0·1935	318·60	3·405
Mean ..			<u>3·4045</u>

From the former experiments we get the atomic weight 29·37; from these, also 29·37.

Specimen No. 2.

None of this specimen could be found.

Specimen No. 3.

No. of experiment.	Weight of cobalt taken.	Vol. of hydrogen.	Weight of hydrogen from 100 pts of cobalt.
1	0·1909	314·73	3·410
2	0·1854	305·40	3·407
			<u>3·4085</u>

From the former experiments the atomic weight is 29·37; from these experiments it is 29·34.

		Atomic Weight.	
		From reduction of the oxide.	From volume of hydrogen evolved.
Specimen No. 1	1st Purification	29·36	29·43
"	2nd Purification	29·37	29·39
"	3rd Purification	29·37	29·37
Specimen No. 2	29·38	—
Specimen No. 3	29·37	29·34
Mean.....		<u>29·37</u>	<u>29·38</u>

NICKEL.

Specimen No. 1.

No. of experi- ment.	Weight of nickel taken.	Vol. of hydro- gen.	Weight of hydrogen from 100 pts. of nickel.
1	0.0906	153.62	3.420
2	0.1017	172.32	3.418
3	0.199	337.06	3.416
4	0.0997	168.93	3.417
5	0.1891	319.86	3.412
6	0.1859	314.75	3.415
7	0.1838	311.25	3.416
Mean			3.416

The former experiments with this specimen gave the atomic weight 29.37; these experiments give 29.27. In experiments 1, 2, 3, and 4, oxide of nickel was taken, reduced, and then dissolved. No. 5 was made with metal which had formerly been used, but was again reduced in hydrogen before dissolving in the hydrochloric acid. Nos. 6 and 7 were made with metal previously used, but not again reduced in hydrogen. In these and the succeeding experiments, $\bar{5}3047564$ represents the logarithm of the weight of one volume of hydrogen.

Specimen No. 2. 3rd Purification.

No. of Experi- ment.	Weight of nickel taken.	Vol. of hydro- gen.	Weight of hydrogen from 100 pts. of nickel.
1	0.1892	318.75	3.398
2	0.1806	305.28	3.409
3	0.2028	333.81	3.404
Mean			3.404

Atomic weight from former experiments, 29.36; atomic weight from these experiments, 29.38.

Experiment No. 3 was made when the logarithm of the weight of one volume of hydrogen was $\bar{5}3156213$.

Experiment No. 2 was made with metal which had not been again heated in hydrogen.

Specimen No. 3. 1st Purification.

No. of experiment.	Weight of nickel taken.	Vol. of hydrogen.	Weight of hydrogen from 100 pts. of nickel.
1	0.1933	325.93	3.401
Atomic weight from former experiments ..			29.38
,, ,, this experiment ..			29.40

The experiment was made on some oxide which had not been used, no metal of this first purification remaining.

Specimen No. 3. 2nd Purification.

No. of experiment.	Weight of nickel taken.	Vol. of hydrogen.	Weight of hydrogen from 100 pts. of nickel.
1	0.1890	319.77	3.412
2	0.1942	328.15	3.408
3	0.1781	301.09	3.410
Mean			3.410

Atomic weight from former experiments.. 29.37

,, ,, these ,, .. 29.33

In experiment No. 3 the metal was not heated in hydrogen before dissolving in the hydrochloric acid.

		Atomic weight.	
		From reduction of oxide.	From vol. of hydrogen evolved.
Specimen No. 1	29.37	29.27
Specimen No. 2	3rd Purification	29.36	29.38
Specimen No. 3	1st Purification	29.38	29.40
Specimen No. 3	2nd Purification	29.37	29.33
Mean		29.37	29.35

The President remarked that it was very satisfactory to find Dr. Russell's present experiments giving results which agreed so closely with those he had formerly obtained by a perfectly independent process.

Professor Wanklyn reminded the Society that in 1866 Mr. Chapman and himself had communicated determinations of the quantity of hydrogen evolved by the solution of metallic

magnesium, which were better determinations of the equivalent of that metal than those obtained by other processes, and that they had suggested that this might be an accurate method of determining the equivalents of the metallic elements generally. It was very satisfactory to him to find that their estimate of the value of this method was confirmed by Dr. Russell.

Dr. Russell said that Gay-Lussac had determined the atomic weight of iron by this method.

XXVI.—*On Ethyl-hyposulphurous Acid.*

By R. H. SMITH, F.C.S.

Part I.

THE hyposulphites possessing considerable interest to the chemist, I have endeavoured to prepare some salts which may be classed under their category, in which an alcohol radicle is introduced as one of the constituents. For this purpose I commenced by preparing ethylic sulphide; and as the yield of this substance is generally very small, it may be worth while to relate briefly the mode adopted for its preparation.

Protosulphide of potassium was placed in a retort with ordinary alcohol, while a tube conveying the vapour of ethylic chloride, as it was formed (by the action of sulphuric acid and alcohol upon common salt) passed into the liquid; after about half hour or so, heat was applied to the retort, when a distillate, having the odour of garlic and rotten cabbage, came over, which contained ethylic sulphide, alcohol, and ethylic chloride. Water was now added, and the oil which separated was redistilled; after rectification over calcium chloride, it was found to have a constant boiling point at 81° C.

As there are such discrepancies in the different manuals of chemistry with regard to the boiling point of this substance, it may be well to remark here that some considerable quantity of the oil was made, and found to boil with great regularity. Where its boiling point is given as low as 73° C., as in Watts's Dictionary, it has probably been contaminated with ordinary alcohol.

About six ounces of the ethylic sulphide was treated with an

equal bulk of strong sulphuric acid; the oil acquired a bright red colour, and a decided fluorescent appearance was produced. A large quantity of water was added, the whole was neutralized with *pure* barium-carbonate, and filtered from the insoluble sulphate; and the resulting solution of barium-ethyl-hyposulphite was evaporated down to about one-third of its bulk, and set aside to crystallise.

In a few days, beautiful colourless, transparent crystals had separated, very regular in form, consisting of nearly, if not quite, rectangular plates, with truncated angles, which, when lying flat, depolarized strongly.

After another crystallisation from water, the crystals were dried in vacuo, and submitted to analysis, with the following results:—

- I. 0·3809 grm. substance, burnt with lead-chromate and oxygen gas, gave 0·1483 grm. carbonic dioxide, and 0·1175 grm. water.
 II. 0·2875 grm. substance, precipitated with dilute sulphuric acid, gave 0·150 grm. ignited barium-sulphate.
 III. 0·405 grm. substance gave 0·2105 grm. barium-sulphate.

		Theory.	I.	II.	III.
C ₄ 48	10·54	10·62		
H ₁₄ 14	3·08	3·42		
Ba 137·18	30·14		30·67	30·37
S ₄ 128	28·12			
O ₈ 128	28·12			
	<hr/> 455·18	<hr/> 100·00			

It will be seen that the numbers obtained correspond very closely with those required by the formula $(C_2H_5)_2Ba''S_4O_6 + 2H_2O$, and that the body in question is analogous to that described by Dr. Stenhouse in the phenyl series. Barium-ethyl-hyposulphite is very soluble in water, but not so readily soluble in alcohol.

Copper-Salt.—This was prepared from the barium-salt by adding a known quantity of cupric sulphate; it forms small square platy crystals, which, like the barium-compound, are very soluble in water.

I have also prepared the *silver-* and *sodium-salts*; the former crystallises in small shining scales; the latter does not appear to crystallise well.

I hope before long to bring before the Society some experiments on methyl- and amyl-hyposulphites, and to show how these bodies are built up, and whether when a metal is introduced into the compound they should be viewed as double salts or not. It is possible such salts as these may throw light upon the constitution of hyposulphurous acid.

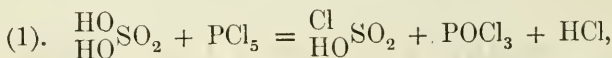
Sheffield, June 1st, 1869.

The President, alluding to the discussion of the constitution of the hyposulphites which had taken place at a recent meeting of the Society,* said that Mr. Smith's results did not appear to him to bear very directly upon the question which had then been raised,—namely, whether any of the water contained in the crystallised hyposulphites, and commonly regarded as water of crystallisation, really belonged to the molecule of the salt,—for the compounds obtained by Mr. Smith bore exactly the same relation to the ordinary hyposulphites that the sulphovicates did to the ordinary sulphates.

XXVII.—On Chlorhydrated Sulphuric Acid.

By the Rev. STEPHEN WILLIAMS, Professor of Chemistry in Stonyhurst College.

It will be recollected that about fourteen years ago, Professor Williamson discovered that by acting on hydric sulphate with phosphoric chloride, chlorhydrated sulphuric acid was produced. In his hands this reaction became very important from a theoretical point of view, and went far to establish the theory of types. He explained it as the replacement of half the hydroxyl in hydric sulphate by univalent chlorine, thus—

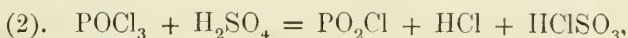


the chlorhydrate being formed together with phosphoric oxichloride and hydric chloride.

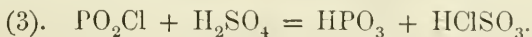
* Pages 254—259 of this volume.

My colleague, the Rev. J. MacLaurin, in preparing some of this chlorhydrate, called my attention to a well-defined crystalline body in the neck of the retort. This anomaly determined me, as time did not permit him to continue the work, to investigate more fully the reaction of phosphoric chloride and hydric sulphate.

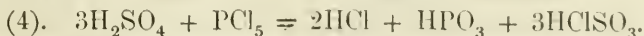
In the first instance an excess of hydric sulphate was used, and the yield of chlorhydrate was small. After all the chlorhydrate had been distilled over, a liquid followed which, when cool, crystallised in the ordinary form, and was found to possess all the properties of sulphuric acid, SO_3 . On raising the temperature, a distillate was obtained which crystallised in plates exactly similar to those obtained by Mr. MacLaurin. As these last crystals could not then be freed from adhering liquid, the analysis was thought inadvisable. But qualitative observation has shown the probability that they are a definite hydrate of sulphuric acid containing more acid than Nordhausen sulphuric acid. The residue in the retort was next submitted to examination, and, after evaporating the excess of hydric sulphate, the glacial metaphosphate remained. The reaction, therefore, was shown to go further than was originally found by Dr. Williamson. As the distillate on decomposition with water was found to contain no phosphate, it was clear that the phosphoric oxichloride first formed again reacted on the hydric sulphate. This may be represented in two successive steps:—



and then

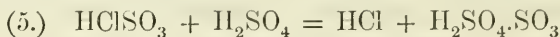


It was found that the chlorhydrate was yielded in the largest quantities when the substances were used in proportions corresponding to three molecules of hydric sulphate to one of phosphoric chloride, a slight excess of hydric sulphate being added to ensure the complete decomposition of the phosphoric oxichloride. The whole reaction may be represented then by the equation—



When a very large excess of hydric sulphate was used, no chlorhydrate was obtained, but hydric chloride was given off in great quantities followed by sulphuric acid SO_3 .

The fact of sulphuric acid being obtained was explained by the discovery that the chlorhydrate is broken up by normal hydric sulphate, hydric chloride being given off with great violence, and Nordhausen acid being left.



Having prepared a quantity of the chlorhydrate which gave a satisfactory analysis,

	Calculated.	Found.	
SO_3	68·67	—	69·20
HCl	31·33	31·28	30·72
	<hr/> 100·00		<hr/> 99·92

it was determined to take its vapour-density. This was done by Dumas's method, as the substance attacks mercury with great energy.

The first determination gave the following results:—

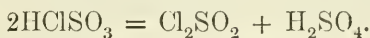
Calculated density	
$\text{HClSO}_3 = 4$ vols.	Found.
29·125	48·813

There were many reasons for doubting the accuracy of this determination. Firstly, the bulb was shown not to be absolutely free from moisture, as some of chlorhydrate was decomposed on entering; secondly, too much of the liquid was taken; and lastly, the analysis of the contents of the globe gave 78·241 per cent. SO_3 instead of 68·721, showing that probably decomposition had taken place from the presence of moisture. Another determination was accordingly made. The bulb was sealed at 216°C ., *circa* 71° above the boiling-point of the liquid. The numbers corresponded to about $3\frac{1}{2}$ volumes.

Calculated density	
$\text{HClSO}_3 = 4$ vols.	Found.
29·125	32·857

This result confirmed the surmise founded on its analogy to hydric sulphate, that in the state of vapour it breaks up into hydric chloride and sulphuric acid. To separate the mixed vapour into its constituents, diffusion was attempted. Many forms of apparatus were tried, but without success, and as yet the separation has not been effected. The mere fact that small quantities of hydric chloride are liberated would not be evidence that diffusion was taking place. For Dr. Williamson has

proved that by continued heating the chlorhydrate is decomposed into chlorosulphuric acid and hydric sulphate, thus—



Now, this hydric sulphate would, as has been shown, break up some chlorhydrate, setting free hydric chloride, and retaining the sulphuric acid. This difficulty, however, is not insurmountable.

This investigation was carried on in the laboratory of University College, London, under the direction of Dr. Williamson.

XXVIII.—*Apparatus for determining the quantities of Gases existing in Solution in Natural Waters.*

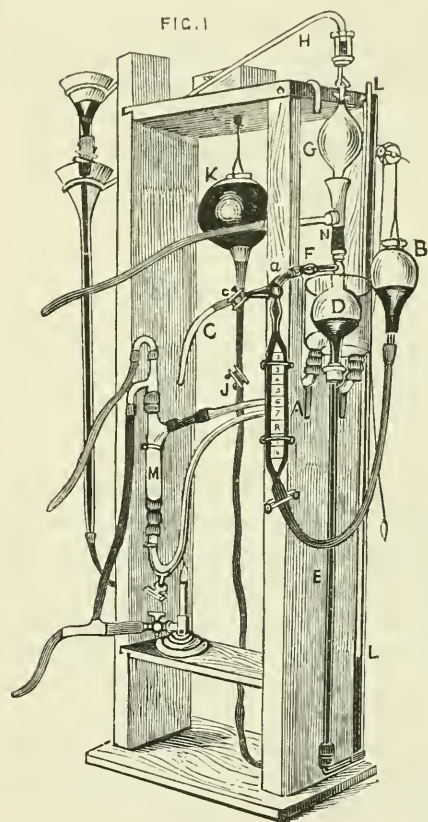
By HERBERT M^cLEOD.

THE object of the following apparatus is to remove the gases existing in solution in natural waters, so as to prevent them, after elimination, from coming in contact with any cold water, which might absorb some of the carbonic anhydride, and thus produce a loss in its estimation. The dissolved oxygen may also be removed from the water at a low temperature, and thus be prevented from acting on any organic or other matter which may be present.

The apparatus consists essentially of three parts:—1. The measuring tube; 2. The flask in which the boiling of the water is carried on; and, 3. The Sprengel's mercurial air-pump to remove the gases after they have been evolved from the water.

The measuring tube consists of a graduated pipette, A (Fig. 1), holding 100 c.c., the lower end of which is connected to a globe, B, by means of a piece of caoutchouc tube sufficiently long to allow the globe to be raised above the level of the top of the pipette. To the upper part of the graduated tube is sealed a piece of narrower glass tube contracted at one point, *a*, and which, above the contraction, is bent at an obtuse angle. Below the contraction another piece of tube is sealed, and this is also narrowed as near to the junction as possible. This lateral tube is joined by means of a caoutchouc

connector provided with a compression cock to a narrow tube, C, which is bent near to its upper extremity, so that the remaining portion hangs almost perpendicularly.



The flask, D, in which the boiling of the water is carried on, consists of a thin glass globe of a capacity of about 150 c.c., with two openings, the lower of which is adapted to a narrow glass tube, E, of about 800 mm. in length, and to the upper opening of the flask a wide tube is joined. A glass stopcock, F, is sealed into the side of this tube, and is connected, by a short piece of caoutchouc bound with wire, to the tube at the top of the measuring tube. The glass tubes within the connector must be in close contact. The upper end of the wide tube is joined to a narrow one, which, by means of a caoutchouc connector, surrounded by mercury, N, is in communication with another globe, G, of nearly the same capacity as the

previous one. The tube at the lower part of this second globe should not exceed 1 mm. in internal diameter. A good glass stopcock is sealed to the top of the second globe, and this is connected by means of a joint of india-rubber surrounded with glycerin to the Sprengel's air-pump.

The lower of the two globes just described is placed in an inverted three-necked Woulfe's bottle, from which the bottom has been removed; through the centre tubulure the long tube, E, is passed, the two other tubulures being connected together by means of a piece of composition gas-tubing. The inverted

Woulfe's bottle is filled with water which may be heated by placing a gas flame beneath the metal tube. To the lower end of the long tube, E, is fastened a piece of narrow caoutchouc tube, covered with tape, and long enough to allow the reservoir K to be raised to the level of the upper flask. This reservoir, and also the one in communication with the measuring tube, are suspended by cords, so that they can readily be raised to any required height. Between the tubes E and J, it is convenient to adapt a long perpendicular glass tube L, open at the top, which serves to indicate the pressure within the globes.

In order to use the apparatus, it has to be filled with mercury. For this purpose mercury is poured into the globe, B, and the globe raised until the metal fills the measuring tube and flows out from the narrow tube C. The compression-cock *c* is closed, and mercury is allowed to pass through the stopcock into the boiling flask; when the air has been expelled, the stopcock is shut. Mercury is also poured into the reservoir K so as to expel the air through the stopcock and Sprengel-pump. The Sprengel is then put in action until the connecting tube is filled with mercury, when the stopcock is closed.

The water has next to be measured. To do this, the narrow tube C is passed to the bottom of the bottle containing the water, the reservoir depressed below the level of the extremity of the narrow tube, and the compression-cock *c* gently opened. It is perhaps more advantageous to fully open the compression cock; but, in order to prevent the water from flowing in too rapidly, the passage of the mercury through the caoutchouc-tube into the reservoir is checked. In cases of waters strongly charged with gas, this latter method diminishes the quantity of gas which escapes from the water during its introduction into the measure, and which would, of course, produce an error in the measurement of the liquid. Usually 100 c.c. of water is a convenient quantity to use, but in some cases a much smaller quantity will suffice. When the measurement of the water is completed, the cock *c* is closed and the reservoir B again raised.

A Torricellian vacuum is next produced in the two flasks by lowering the reservoir K until only a small quantity of mercury remains in the lower globe. A compression-cock on the caoutchouc tube J is then closed, and, to avoid any loss which might be occasioned by leakage through the compression-cock, the

reservoir is raised to its original position. The stopcock of the measuring tube is now opened and the water passed into the lower globe, the water in the inverted Woulfe's bottle being maintained as nearly as possible at 50° . The temperature can be kept very nearly constant by means of a thermostat M, placed in the circulating tube; a thermometer, not shown in the figure, being placed in the bath. After a few drops of mercury have been allowed to flow into the flask, the stopcock is turned and the water left for thirty minutes *in vacuo* at 50° . During this time almost the whole of the oxygen which was dissolved in the water will be expelled. This should always be done before raising the temperature to the boiling point, in order to avoid any absorption of the gas by organic matter that the water may contain. To remove the gas from the apparatus, the compression-cock on the long tube J is opened, and the mercury allowed to rise into the flasks. The stopcock is gently opened so as to permit the gas to pass into the Sprengel. When the water has nearly reached the stopcock, the latter is closed, and the reservoir lowered so as once more to produce a vacuum above the water in the globes; the reservoir is again raised and the whole of the gas passed through the Sprengel, the stopcock being turned when the water just reaches it. The reservoir is once more lowered, and the water in the bath heated as far as possible; a piece of rag is placed round the upper flask and a stream of cold water caused to run on to it, the excess of water being collected by the funnel-shaped head of the mercury-joint surrounding the connector N, and escaping through the lateral tube. The water in D rapidly distils into the upper flask, and is prevented from returning to the lower by the narrowness of the connecting tube.

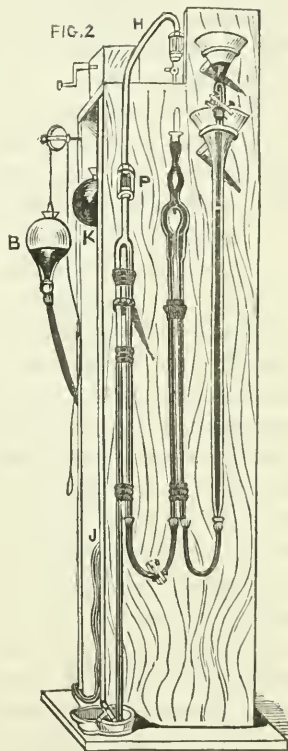
Before commencing the distillation, it is advisable to fill the tube H, above the stopcock, with mercury; this can easily be done by causing the mercury to pass very rapidly through the Sprengel, when some of it rises into the vacuous tube.

When the water has entirely evaporated from the lower flask, mercury is allowed to flow in, and the gas is transferred as before.

As some carbonic anhydride still remains dissolved in the water, the liquid must be again passed into the globe D, by lowering the reservoir K, and the water in the bath heated to boiling and maintained at that temperature for a few minutes.

The remainder of the carbonic anhydride is thus expelled, and is removed by the Sprengel.

A few words may here be said on the form of mercurial pump (Fig. 2) used for this apparatus. This is slightly modified from the invaluable instrument for which chemists and physicists are so deeply indebted to Dr. H. Sprengel, and described by him a few years ago*. A piece of thick glass tube about 8 feet in length, and 1 mm. internal diameter, is bent at a distance of 3 feet from one of its ends. The bend is made as sharp as possible, and the tubes are firmly bound together with copper wire at two points. To the top of the bend a piece of straight tube is sealed and connected by a joint, P, surrounded by glycerin, with the tube communicating with the apparatus. The end of the longer limb of the pump is curved so as to act as a delivery tube, the shorter one communicating with the tube supplying the mercury by means of a piece of caoutchouc tube covered with tape. By this arrangement the pump is perfectly movable, being merely held in the perpendicular position by a support at the upper part, the lower end resting on the bottom of the mercurial trough. The pump is also provided with an apparatus for removing any air entangled or dissolved in the mercury, which will soon be fully described by Dr. Sprengel, by whom it was kindly suggested. This form of pump has been found to work very satisfactorily, the best exhaustion measured being $\frac{1}{516.366}$ th of the original volume of air in the receiver. This, however, is much inferior to that obtained by Dr. Sprengel with his original apparatus, which amounted to $\frac{1}{1.300.000}$ th. By means of a pump of this form, Dr. Frankland and Mr. Lockyer, in their experiments on the spectra of gases, have rarefied perfectly dry oxygen, nitrogen, and hydrogen, to such an extent,



* Journ. Chem. Soc., vol. xviii (N.S., vol. iii), p. 9.

that they possessed a resistance to the spark of the induction coil equal to that of the atmosphere; and since then a tube has been prepared containing a residue of air of a resistance seventy-five times as great as that of moist air, at the ordinary pressure and temperature.

By careful management, only very small quantities of liquid water pass over with the gas, there being usually only sufficient to moisten the sides of the receiver, a quantity which would not produce any appreciable loss of carbonic anhydride.

The gas evolved at 50° may be analysed either separately, or first mixed with that given off on distillation. It was hoped that, by removing the gas at two different temperatures, a separation might be effected between the gases dissolved and those combined; but it appears that the dihydric calcic dicarbonate is slowly decomposed even at 50°. Small quantities of oxygen and nitrogen are also invariably found in the gases evolved on distillation: and in an experiment made with a solution of carbonic anhydride in distilled water, only a portion of the gas, amounting, however, to nearly $\frac{1}{2}\%$ ths, escaped from the solution at 50° in 30 minutes. It has been found very difficult to decompose the dihydric calcic dicarbonate by boiling the water: even after the temperature had been maintained at 105°—108°, for two or three hours it was found that the whole of the carbonic anhydride had not been evolved. It may, however, be presumed that the carbonate will not remain undecomposed when the water is evaporated to dryness.

The following results have been obtained in the determination of the gases in 100 volumes of Grand Junction water, as drawn from the cistern at the Royal College of Chemistry:—

I.

	Evolved at 50°.	Evolved on distillation.	Total.
Nitrogen.....	1·391	0·007	1·398
Oxygen	0·609	0·011	0·620
Carbonic anhydride	0·420	3·877	4·297
	<hr/> 2·420	<hr/> 3·895	<hr/> 6·315

II.

	Evolved at 50°.	Evolved on dis- tillation.	Total.
Nitrogen.....	1·396	0·002	1·398
Oxygen	0·606	0·013	0·619
Carbonic anhydride	0·499	3·681	4·180
	<hr/> 2·501	<hr/> 3·696	<hr/> 6·197

Determination of gases in rain that fell on July 28, 1869,
between 10 a.m. and noon:—

I.

	Evolved at 50°.	Evolved on dis- tillation.	Total.
Nitrogen.....	1·348	0·033	1·381
Oxygen	0·671	0·014	0·685
Carbonic anhydride	0·045	0·071	0·116
	<hr/> 2·064	<hr/> 0·118	<hr/> 2·182

II.

	Evolved at 50°.	Evolved on boiling (not distilled).	Total.
Nitrogen.....	1·344	0·039	1·383
Oxygen	0·651	0·010	0·661
Carbonic anhydride	0·065	0·090	0·155
	<hr/> 2·060	<hr/> 0·139	<hr/> 2·199

These experiments were conducted at the Royal College of
Chemistry.

XXIX.—*On a new Form of Apparatus for Gas Analysis.*

By HERBERT M^cLEOD.

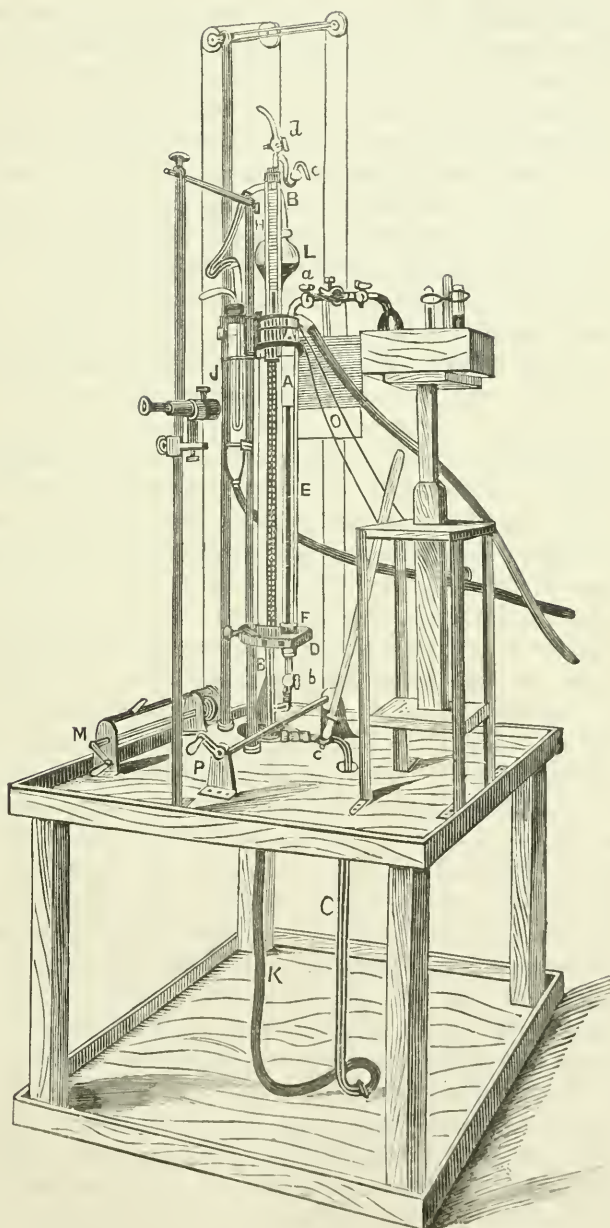
THIS apparatus is merely a modification of the one described
some years ago* by Dr. Frankland and Mr. Ward, by which
the temperature and tension of fixed volumes of gas are mea-
sured, whence the absolute volumes at the standard tempera-
ture and pressure may, if necessary, be calculated.

* Journ. Chem. Soc., vol. vi, p. 197.

The measuring tube A is 900 mm. in length, and about 20 mm. in internal diameter. It is marked with ten divisions, the first at 25 mm. from the top, the second at 50, the third at 100, and the remaining ones at intervals of 100 mm. In the upper part of the tube, platinum wires are sealed, and it is terminated by a capillary tube and fine glass stopcock, *a*, the capillary tube being bent at right angles at 50 mm. above the junction. At the bottom of the tube, a wide glass stopcock *b* is sealed, which communicates, by means of a caoutchouc joint surrounded with tape and well wired to the tubes, with a branch from the barometer-tube B. This latter tube is 5 mm. in width, and about 1,200 mm. long, and is graduated in millimeters from bottom to top. At the upper extremity a glass stopcock *d* is joined, the lower end being curved and connected by caoutchouc with a stopcock and tube C, descending through the table to a distance of 900 mm. below the joint. It is advisable to place washers of leather at the end of the plugs of the stopcocks *c* and *b*, as the pressure of the mercury which is afterwards to be introduced has a tendency to force them out; and if this should happen, the washers prevent any great escape of mercury.

The two tubes are firmly held by a clamp D, on which rests a wide cylinder E, about 55 mm. in diameter, surrounding the tubes, and adapted to them by a water-tight caoutchouc cork F. The cylinder is maintained in an upright position by a support at its upper end G, sliding on the same rod as the clamp. Around the upper part of the barometer-tube a syphon H is fixed by means of a perforated cork, through which the stopcock *d* passes. A small bulb-tube *e*, containing some mercury, is also fitted in this cork, so as to allow of the air being entirely removed from the syphon. The syphon descends about 100 mm. within the cylinder, and has a branch at the top communicating by caoutchouc with a bent tube contained in a wider one J affixed to the support. A constant current of water is supplied to the cylinder through a glass tube, which passes to the bottom, and escapes through the syphon and tubes to the drain.

To the end of the narrow tube C, is fastened a long piece of caoutchouc tube K, covered with tape, by which a communication is established with the mercurial reservoir L, suspended by a cord, so that by means of the winch M, it may be raised



above the level of the top of the barometer-tube. As the mercury frequently forces its way through the pores of the caoutchouc tube, it is advisable to surround the lower part with a piece of wide flexible tube; this prevents the scattering of the mercury, which collects in a tray placed on the floor. Into the bottom of the tray a screw must be put, to which the end of the glass tube is firmly attached by wire. The capillary stopcock *a* is provided with a steel cap, by means of which it may be adapted to a short and wide laboratory-tube capable of holding about 150 c.c., and identical in form with the one described last year* by Dr. Frankland. The mercurial trough for the laboratory-tube differs from that employed by Dr. Frankland, only, by being a little wider, and by having a stand with rings for the purpose of holding two tubes containing gases that may be required.

The apparatus is used in the same way as the original one, except that the mercury is raised and lowered in the tubes by the movement of the reservoir, *L*, instead of pouring it into the centre supply-tube, which is dispensed with in the present apparatus.

To arrange the apparatus for use, the reservoir *L* is lowered to the ground, and mercury poured into it. The laboratory-tube being removed, the stopcocks are all opened, and the reservoir gradually raised. When the tube *A* is filled, the stopcock *a* is closed, and the reservoir elevated until mercury flows through the stopcock *d* at the top of the barometer tube. It is convenient to have the end of the tube above the stopcock so bent that a vessel can be placed below to receive the mercury. This bend must, of course, be so short that, when the plug of the stopcock is removed, the syphon will pass readily over. When the air is expelled from the barometer-tube, the stopcock is closed. A few drops of water must next be introduced into the barometer; this is accomplished by lowering the reservoir to a short distance below the top of the barometer, and gently opening the stopcock *d*, while a small pipette, from which water is dropping, is held against the orifice, the stopcock being closed when a sufficient amount of water has penetrated into the tube. In the same manner, a small quantity of water is passed into the measuring tube. In order to get rid of any bubbles of air which may still linger

* Journ. Chem. Soc., vol. xxi (New Series, vol. vi), p. 109.

in the tubes, the reservoir is lowered to the ground so as to produce a vacuum in the apparatus; in this manner the interior surfaces of the tubes become moistened. The reservoir is now gently raised, thus refilling the tubes with mercury. Great care must be taken that the mercury does not rush suddenly against the tops of the measuring- and barometer-tubes, which might cause their destruction; this may be avoided by regulating the flow of mercury by means of the stopcock *c*, which may be conveniently turned by a long key of wood, resting against the upper table of the sliding stand of the mercurial trough. When the reservoir has again been elevated above the top of the barometer, the stopcocks of the measuring and barometer tubes are opened, and the air and water which have collected allowed to escape.

The heights of the mercurial columns in the barometer corresponding to the different divisions of the measuring tube, have now to be determined. This is done by running out all the mercury from the tubes, and slowly readmitting it until the meniscus of the mercury just touches the lowest division in the measuring tube. This may be very conveniently managed by observing the division through a small telescope of short focus, and sufficiently close to the apparatus to permit of the key of the stopcock *c* being turned, while the eye is still at the telescope. When a reading is taken, the black screen *O* behind the apparatus, must be moved by means of the winch *P*, until its lower edge is about a millimeter above the division. The telescope is now directed to the barometer-tube, and the position of the mercury carefully noted. As the tubes only contain aqueous vapour, and are both at the same temperature, the columns in the two tubes are those which exactly counterbalance one another, and any difference of level that may be noticed is due to capillarity. The same operation is now repeated at each division of the tube. The measuring tube next requires calibration, an operation performed in a manner perfectly similar to that described in Dr. Frankland's paper of last year, already quoted, namely, by filling the measuring tube with water, and weighing the quantities contained between every two divisions. The endiometer being filled with water, and the stopcock *b* closed, the reservoir is raised and the mercury allowed to rise to the top of the barometer. The capillary stopcock *a* having been opened, the cock *b* is gently turned, and

the water allowed to flow out until the mercury reaches the lowest division of the tube. A carefully-weighed flask is now supported just below the steel cap, the stopcock *b* again opened, until the next division is reached, and the quantity of water is weighed, the temperature of the water in the wide cylinder being observed. The same operation is repeated at each division, and by calculation the exact contents of the tube in cubic centimeters may be found.

In this manner a table, such as the following, is obtained :—

Division on measuring tube.	Height of mercury in barometer-tube, corresponding to division.	Contents.	
		Cubic centimeters.	Log.
1	756.9	8.6892	0.9389814
2	706.7	18.1621	1.2591664
3	606.8	36.9307	1.5673880
4	506.5	55.7344	1.7461232
5	406.8	74.4299	1.8717477
6	306.8	93.3306	1.9700244
7	206.9	112.4165	2.0508303
8	107.0	131.6335	2.1193666
9	7.1	151.1623	2.1794435

When a gas is to be analysed, the laboratory-tube is filled with mercury, either by sucking the air out through the capillary stopcock, while the open end of the tube stands in the trough, or much more conveniently, by exhausting the air through a piece of flexible tube passed under the mercury to the top of the laboratory-tube, the small quantity of air remaining in the stopcock and at the top of the wide tube being very readily withdrawn. The face of one of the steel pieces is greased with a small quantity of resin cerate, and, the measuring apparatus being full of mercury, the clamp is adjusted.

Before the introduction of the gas, it is advisable to ascertain if the capillary tubes are clear, as a stoppage may arise from the admission of a small quantity of grease into one of them. For this purpose the globe *L* is raised above the level of the top of the measuring tube, and the capillary stopcocks opened; if a free passage exists, the mercury will be seen to flow through the tubes. The stopcock of the laboratory tube is now closed. When all is properly arranged, the gas is transferred

into the laboratory-tube, and the stopcock opened, admitting a stream of mercury. The cock *c* is gently turned so as just to arrest the flow of mercury through the apparatus, and the reservoir lowered to about the level of the table, which is usually sufficient. By carefully opening the cock *c* the gas is drawn over into the measuring tube, and when the mercury has reached a point in the capillary tube of the laboratory-tube, about midway between the bend and the stopcock, the latter is quickly closed. It is necessary that this stopcock should be very perfect. This is attained by grinding the plug into the socket with fine levigated rouge and solution of sodic or potassic hydrate; by this means the plug and socket may be polished so that a very small quantity of resin cerate and a drop of oil renders it perfectly gas-tight. In grinding care must be taken that the operation is not carried on too long, otherwise the hole in the plug may not coincide with the tubes. If this stopcock is in sufficiently good order, it is unnecessary to close the stopcock *a* during an analysis.

The mercury is allowed to flow out of the apparatus until its surface is a short distance below the division at which the measurements are to be made. The selection of the division depends on the quantity of gas and the kind of experiment to be performed with it. A saving of calculation is effected if all the measurements in one analysis are carried on at the same division. When the mercury has descended below the division, the cock *c* is closed, the reservoir raised, and the black screen moved until its lower edge is about a millimeter above the division, and the telescope placed so that the image of the division coincides with the cross-wires in the eye-piece. The stopcock *c* is now gently opened until the meniscus just touches the division; the cock is closed and the height of the mercury in the barometer is measured by means of the telescope. The difference between the reading of the barometer and the number in the table corresponding to the division at which the measurement is taken, gives in millimeters the tension of the gas. The volume of the gas is found in the same table, and with the temperature, which is read off at the same time as the pressure, all the data required for the calculation of the volume of the gas at 0° and 760 mm. are obtained. No correction is required for tension of aqueous vapour; the measuring tube and barometer-tube being both moist, the tensions in the tubes are

counterbalanced. Absorptions are performed with liquid reagents by introducing a few drops of the liquid into the laboratory-tube, transferring the gas into it and allowing the mercury to drop slowly through the gas for about five minutes. The gas is then passed over into the measuring tube, and the difference of tension observed corresponds to the amount of gas absorbed. It is scarcely necessary to add that the greatest care must be taken to prevent any trace of the reagent passing the stopcock. If such an accident should occur, the measuring tube must be washed out several times with distilled water at the conclusion of the analysis. If the reagent is a solution of potassic hydrate it may be got rid of by introducing into the tube some distilled water, to which a drop of sulphuric acid has been added; if this liquid is found to be acid on removing it from the tube, it may be presumed that all the alkali has been neutralized.

When explosions are to be performed in the apparatus, the gas is first measured and then returned to the laboratory-tube. A quantity of oxygen or hydrogen, as the case may be, which is judged to be the proper volume, is transferred into the laboratory tube, and some mercury is allowed to stream through the gases so as to mix them thoroughly. The mixture is next passed into the eudiometer and measured. If a sufficient quantity of the second gas has not been added, more can readily be introduced. After the measurement, it may be advisable to expand the mixture, in order to diminish the force of the explosion. This is done by allowing mercury to flow out from the tube into the reservoir. When the proper amount of expansion has been reached, the stopcocks *a* and *b* are closed. To enable the electric spark to pass between the wires, it is necessary to lower the level of the water in the cylinder. For this purpose the bent glass tube at the extremity of the syphon is made to slide easily through the cork which closes the top of the wide tube *J*. By depressing the bent tube, the water flows out more rapidly than before, and the level consequently falls. When the surface is below the eudiometer-wires, a spark from an induction-coil is passed, exploding the gas. The syphon tube is immediately raised, and, when the water in the cylinder has reached its original level, the gas is cool enough for measurement.

The following details of an analysis, in which absorptions

only were performed, will show the method employed. The gas was a mixture of nitrogen, oxygen, and carbonic anhydride, and the measurements were all made at division No. 1 on the eudiometer, which had been found to contain 8.6892 c.c.

ORIGINAL GAS.

Temperature of water in cylinder, 15.4°.

	mm.
Height of mercury in barometer-tube	980.5
" " corresponding to Division No. 1	
(see Table)	756.9
Tension of the gas.....	<u>223.6</u>

After absorption of the carbonic anhydride by solution of potassic hydrate—

Height of mercury in barometer-tube	941.7
" " corresponding to Division No. 1..	756.9
Tension of the gas after removal of carbonic anhydride..	<u>184.7</u>
Tension of original gas	223.6
" gas after removal of carbonic anhydride....	184.8
Tension of carbonic anhydride.....	<u>38.8</u>

After absorption of the oxygen by potassic pyrogallate—

Height of mercury in barometer-tube.....	885.4
" " corresponding to Division No. 1....	756.9
Tension of nitrogen	<u>128.5</u>
Tension of oxygen and nitrogen	184.8
" nitrogen	128.5
" oxygen.....	<u>56.3</u>

These measurements, therefore, give us the following numbers :—

	mm.
Tension of nitrogen	128.5
„ oxygen.....	56.3
„ carbonic anhydride.....	38.8
„ original gas.....	223.6

If the percentage composition of the gas is required, it is readily obtained by a simple proportion, the temperature having remained constant during the experiment:—

mm.	mm.	mm.	
223.6	: 128.5	:: 100	: 57.469 per cent. N.
223.6	: 56.3	:: 100	: 25.179 „ O.
223.6	: 38.8	:: 100	: 17.352 „ CO ₂
<hr/>			
100.000			

If, however, it is necessary to calculate the number of cubic centimeters of the gases at 0° and 760 mm., it is done by the following formulæ:—

$$\begin{aligned} \frac{8.6892 \times 128.5}{760 \times [1 + (0.003665 \times 15.4)]} &= 1.3906 \text{ c.c. of nitrogen.} \\ \frac{8.6892 \times 56.3}{760 \times [1 + (0.003665 \times 15.4)]} &= 0.6093 \text{ c.c. of oxygen.} \\ \frac{8.6892 \times 38.8}{760 \times [1 + (0.003665 \times 15.4)]} &= 0.4199 \text{ c.c. of carbonic anhydride.} \\ \frac{8.6892 \times 223.6}{760 \times [1 + (0.003665 \times 15.4)]} &= 2.4198 \text{ c.c. of the original gas.} \end{aligned}$$

If many of these calculations are to be done, they may be very much simplified by constructing a table containing the logarithms of the quotients obtained by dividing the contents of each division of the tube by $760 \times (1 + 0.003665 t)$. The following is a very short extract from such a table:—

T°.	Division No. 1.	Division No. 2.
	Log. $\frac{8.6892}{760 \times (1 + \delta t)}$	Log. $\frac{18.1621}{760 \times (1 + \delta t)}$
15.0	$\bar{2}.03492$	$\bar{2}.35511$
•1	$\bar{2}.03477$	$\bar{2}.35496$
•2	$\bar{2}.03462$	$\bar{2}.35481$
•3	$\bar{2}.03447$	$\bar{2}.35466$
•4	$\bar{2}.03432$	$\bar{2}.35451$

By adding the logarithms of the tensions of the gases to those in the above table, the logarithms of the quantities of gases are obtained, thus:—

Log. corresponding to Division No. 1, and 15.4°	$\bar{2}.03432$	
Log. 128.5 = tension of nitrogen	$\bar{2}.10890$	
	<hr/>	
Log. of quantity of nitrogen	0.14322	= log. 1.3906
Volume of nitrogen at 0° and 760 mm.	1.3906	c.c.
	<hr/>	
	$\bar{2}.03432$	
Log. 56.3 = tension of oxygen	1.75051	
	<hr/>	
Log. of quantity of oxygen	$\bar{1}.78483$	= log. 0.6093
Volume of oxygen at 0° and 760 mm.	0.6093	c.c.
	<hr/>	
	$\bar{2}.03432$	
Log. 38.8 = tension of carbonic anhy- dride	1.58883	
	<hr/>	
Log. of quantity of carbonic anhydride. .	$\bar{1}.62315$	= log. 0.4199
Volume of carbonic anhydride at 0° and 760 mm.	0.4199	c.c.
	<hr/>	
	$\bar{2}.03432$	
Log. 223.6 = tension of original gas ..	2.34947	
	<hr/>	
Log. of quantity of original gas	0.38379	= log. 2.4198
Vol. of original gas at 0° and 760 mm.	2.4198	c.c.
Nitrogen	1.3906	or 1.391 c.c.
Oxygen	0.6093	or 0.609 „
Carbonic anhydride	0.4199	or 0.420 „
	<hr/>	
Total	2.4198	or 2.420 „

The apparatus above described was constructed at the Royal College of Chemistry, about twelve months ago, and has been in frequent use since that time, always performing its work satisfactorily, and up to the present without the slightest difficulty. 900 c.c. of mercury are amply sufficient for the whole apparatus; and as there is no cement used to fasten the wide tubes into iron sockets, a great difficulty in the original apparatus is avoided.

The measurement and analysis of gases deserve much attention on the part of chemists; there being greater delicacy in measuring than in weighing gaseous bodies, and many analyses, as has been shown by Dr. Russell,* may be performed by the measurement of the gaseous products of certain reactions. The analysis of carbonates, for instance, may be very readily performed by means of a wide barometer-tube with a stopcock at the upper extremity and a Sprengel pump. A small quantity of a carbonate is weighed in a piece of glass tube, open at one end, and with a small hole in the side. This is placed within the barometer-tube, which is then plunged in mercury. The air is exhausted from the tube by means of the Sprengel, and dilute sulphuric or hydrochloric acid passed up into the tube by means of a bent pipette. The tube is warmed by a gas flame, and the gas exhausted by the Sprengel and measured. Only four experiments have, up to the present, been made with this apparatus; these gave the following results:—

	I.	II.
Carbonic anhydride in sodic carbonate (per cent.)	37·66	37·90
„ „ calcic „ (per cent.)	43·72	43·61

XXX.—*Note on the Absorption Spectra yielded by certain Organic Substances.*

By Dr. T. L. PHIPSON, F.C.S.

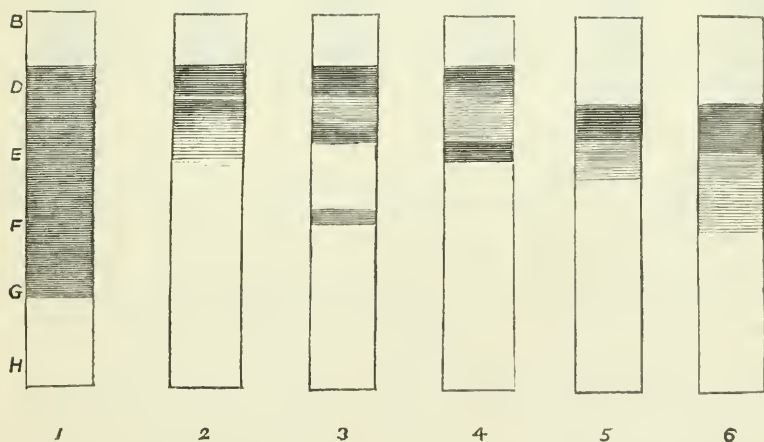
SINCE I published my little paper entitled “*Sur l'Application de certaines propriétés optiques des Corps à l'Analyse Chimique, &c.*,” to which the Royal Society of Medical and Natural Sciences of Brussels, did me the honour to award a gold medal in the competition of 1867, and in which I called attention to the advantages that may be derived by the pharmaceutical, as well as by the analytical chemist, from the use of the prism for the examination of various organic solutions, I have become more convinced every day of the truth of Professor Stokes' observations on this subject previously brought before the Chemical

* Journ. Chem. Soc., vol. xxi (New Series, vol. vi), p. 310.

Society of London; and I believe that the recent observations made by Professor Hoppe, Dr. Gladstone, Professor Stokes, Mr. Sorby, Mr. Crookes, Dr. Reynolds, and others, who have devoted some time to the study of various absorption spectra, will become more valuable as the number of known spectra increases.

In the present short note, I wish to allude only to the principal features presented by solutions of certain organic substances when examined by a prism, perhaps more for their practical than for their scientific interest.

I was rather surprised to find recently that the beautiful chinoline blue, called cyanine, which Mr. Greville Williams, obtained a few years ago as a derivative of the alkaloid cinchonia, gave an absorption spectrum very much resembling that



of mauve—the original aniline dye discovered by Mr. Perkin. When the solutions are somewhat concentrated, they cut out a considerable portion of the spectrum, from beyond the line D to F, or even to G (Fig. 1), but when examined in very dilute solutions they both give a spectrum similar to Fig. 2, namely, a wide dark band just above D, and reaching to this line, and then another band, less dark, below D; these bands often blend one into the other, but with solutions which are not too strong, a faint streak of yellow light finds its way between them. Several substances in commerce, known as Hofmann's violet, mauveine, mauve, aniline pink, or purpurine, and some aniline

greens (but not all the greens sold under that name) show a similar kind of spectrum.

The colours of certain flowers offer absorption bands placed somewhat similarly in the spectrum; for instance, Fig. 3 is that I found presented by *Clarkia pulchella*, which is common in our London gardens; it yields its beautiful violet colour to water and its spectrum is not unlike that of the colouring matter of the flowers of *Lobelia speciosa* (Fig. 4), previously described by Mr. Sorby, which is also soluble in water.

Fig. 5 represents the spectrum of a weak solution of "magenta." It will be seen to differ from the mauve spectrum by the dark band commencing some distance below D, instead of above it; it also presents some similarity to that of the beautiful red colour derived from the flowers of a "Brompton stock," to which a drop of hydrochloric acid is added (Fig. 6).

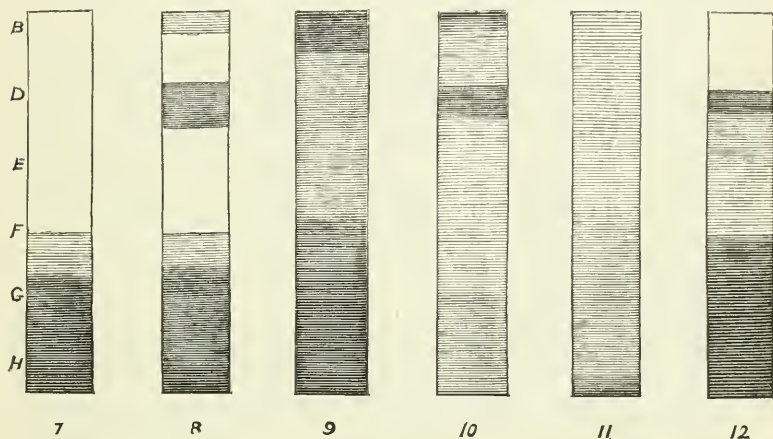
Fig. 7 is the spectrum yielded by solutions of picric acid, picrate of soda, chrysaniline (or the aniline yellow of certain manufacturers), and certain dyes sold under the name of aniline green.

Fig. 8 is the spectrum of a magnificent green solution obtained by mixing picric acid and cyanine. This forms a bright emerald-green solution, and yields a vivid spectrum composed exclusively of red and green.

Many years ago, the celebrated astronomer, William Herschel, spent some time in endeavouring to discover the medium through which the disc of the sun could be studied with the least fear of injury to the eye. After a great number of experiments, he finally arrived at the conclusion that a solution of black writing ink was the substance which should be preferred to all others, and the spectrum of this solution (Fig. 9) shows, indeed, that it must answer the purpose exceedingly well. It is characterized by a general absorption, similar to that which is observed with the colouring matter of the petals of wall-flowers, stocks, and other *cruciferae*, the darkening being more pronounced towards the violet and red extremities of the spectrum.

I have seen it stated that the colouring matter of the purple holyoak, which grows abundantly in Greece, has been used for imitating the colour of wines. Dr. Landerer, professor of chemistry at Athens, was the first, I believe, to call attention to this fact. I imagined that the prism might detect this colour,

and therefore examined the spectrum of the colouring matter in question dissolved in water containing a trace of alum, and that of the grape as seen in a sample of pure Bordeaux wine. The two spectra are seen side by side (Figs. 10 and 11), and it is easy to distinguish them. The pure colouring matter of the



grape gives no absorption bands, but a general absorption, like that of the *cheiranthus* (wall-flower) before mentioned, but gradually darkening towards the violet. With this I compared also the orceine red derived from English lichens (*ramilina*), by the fermentation process, which might be used for a similar purpose. Its spectrum is shown (Fig. 12).

Lastly, I may mention that I have observed the peculiar spectrum recently described by Dr. Thudichum, consisting of three absorption bands between F and H, and ascribed by him to a yellow substance called *luteine*, that would appear to exist in the yolk of eggs and in the petals of many flowers.

I find that the flowers of *Cytisus racemosus*, the colouring matter of which is soluble in water, give this luteine spectrum very distinctly.

XXXI.—*On the Atomic Theory.*

By Prof. A. W. WILLIAMSON, Pres. Chem. Soc., F.R.S., &c.

THERE are considerable differences, not to say discrepancies, between the statements made by different chemists on the subject of the atomic theory. In some text books of the science the replacing values of so-called equivalent weights of elements are described as being the atomic weights of those elements, while in the same and in other books, statements are made respecting the principles of the determination of atomic weights which lead to different numbers from those representing the replacing values.

It sometimes happens that chemists of high authority refer publicly to the atomic theory as something which they would be glad to dispense with, and which they are, rather ashamed of using. They seem to look upon it as something distinct from the general facts of chemistry, and something which the science would gain by throwing off entirely.

Thus, in one book we find the statement:—"It appears from this that 2×8 , or 16 parts of oxygen is the smallest quantity of oxygen that can be supposed to enter into the reaction just considered, if we would avoid speaking of fractions of equivalents; and we shall find hereafter that the same is true with regard to all other well defined reactions in which oxygen takes part. Hence, this quantity of oxygen, 16 parts by weight (hydrogen being the unit), is called an indivisible weight, or atomic weight, or one atom of oxygen."

And again:—

"The question whether matter is infinitely divisible, or whether its divisibility is limited, remains, at the present day, in the same state as when it first engaged the attention of the Greek philosophers, or perhaps that of the sages of Egypt and Hindostan long before them."

Another author says:—

"The law of multiple proportions being founded on experimental facts, stands as a fixed bulwark of the science, which must ever remain true; whereas the atomic theory by which

we now explain this great law may possibly, in time, give place to one more perfectly suited to the explanation of new facts."

When we refer to the author's enunciation of this great law, in a paragraph which is referred to as containing a statement of the law, we find it stated that in the compounds of oxygen and nitrogen the oxygen is in the proportion of 1, 2, 3, 4, 5 to one and the same quantity of nitrogen, and that no compounds exist containing any intermediate quantity of oxygen.

Another distinguished chemist also lays down that the atomic weight of each element is made to agree as far as possible with the three following conditions:—

1st. The smallest proportion by weight in which the element enters into, or is expelled from a chemical compound, the weight of hydrogen so entering or leaving a chemical compound being taken as unity.

2nd. The weight of the element in the solid condition, which, at any given temperature, contains the same amount of heat as seven parts by weight of lithium at the same temperature.

3rd. The weight of the element which, in the form of gas or vapour, occupies, under like conditions of temperature and pressure, the same volume is one part by weight of hydrogen.

Now, if we endeavour to determine according to these rules the atomic weight of phosphorus, we may compare the quantity of hydric chloride containing one part by weight of hydrogen with that weight of phosphoric chloride PCl_5 , which contains the same weight of chlorine, viz., $\frac{\text{P}}{5}\text{Cl}$. In this latter com-

pound, $\frac{\text{P}}{5}$ or 6.2 parts of phosphorus, has entered into combination with 35.5 parts by weight of chlorine, instead of one part by weight of hydrogen, which unites with 35.5 of chlorine in forming hydric chloride. 6.2 is, therefore, according to this rule, taken by itself, the atomic weight of phosphorus. We should not be justified in adopting the weight of phosphorus derived from an analysis of the lower chloride, PCl_3 , because the rule directs us to take the smallest proportion, and the proportion of phosphorus in PCl_5 is smaller than in PCl_3 .

If instead of the chloride we take the acid P_2O_5 , or a phosphate such as PO_4Na_3 , and compare them respectively with $5\text{H}_2\text{O}$ and $\text{H}_5\text{Na}_3\text{O}_4$, we obtain the same atomic weight for phosphorus, 6.2. By the second rule (if we interpret it as

meaning the capacity for heat between two given temperatures), we find that seven parts of lithium, if heated from 0°C. to 1°C. , absorb 6.59 degrees of heat, while one part by weight of solid phosphorus absorbs .1885. We have, consequently, the atomic weight 34.9, which, considering the nature of the determinations, may be accepted as a reasonable approach to the atomic weight 31, now adopted by chemists.

According to the third rule, we obtain for phosphorus the atomic weight 62, inasmuch as P^6 occupy in the state of vapour under like conditions the same volume as H^2 .

In the case of all elements, the first rule gives the smallest weight. Thus, calcium, in the calcic nitrate, $\text{Ca}(\text{NO}_3)_2$, replaces hydrogen in hydric nitrate in the proportion of 20 to 1. Oxygen in carbonic oxide replaces hydrogen by marsh-gas in the proportion of 4 to 1; in most of its compounds in the proportion of 8 to 1. Nitrogen in sal ammoniac replaces 5 atoms of hydrogen in the molecules 4HH and HCl , in the proportion of $2\frac{4}{5}$ to 1.

Another distinguished author describes—

- “The law of definite proportions;
- “The law of multiple proportions; and
- “The law of equivalent proportions.”

He subsequently describes the “hypothesis of the atomic constitution of matter,” the word hypothesis being no doubt intended to indicate an opinion on his part that the atomic constitution of matter is open to more doubt than the so-called law of multiple proportions, &c. Again, in another able book we find it stated that to each element is assigned a “particular number, termed its proportionate number, which expresses the least indivisible proportion of the element that is found to enter into a combination,” hydrogen being taken as the unit,—a very intelligible description of the atomic weight of the element. In illustration of these so-called proportional numbers, the author gives Gerhardt’s table of atomic weights, which were in use at the time his work was written. He avoids the word atom in describing his indivisible proportions, although later on he occasionally falls into the use of the common words “atomic weight,” and atom. When he comes to explain molecules and equivalents, there is no more talk about proportional numbers.

It certainly does seem strange that men accustomed to con-

sult nature by experiment so constantly as chemists do, should make use of a system of ideas of which such things can be said. I think I am not overstating the fact, when I say, that, on the one hand, all chemists use the atomic theory, and that, on the other hand, a considerable number of them view it with mistrust, some with positive dislike. If the theory really is as uncertain and unnecessary as they imagine it to be, let its defects be laid bare and examined. Let them be remedied if possible, or let the theory be rejected, and some other theory used in its stead, if its defects are really as irremediable and as grave as is implied by the sneers of its detractors.

But if the theory be a general expression of the best ascertained relations of matter in its chemical changes, the only general expression which those relations have as yet found, and be hypothetical only in so far as it presupposes among unknown substances relations analogous to those discovered among those which are known, then it must be classed among the best and most precious trophies which the human mind has earned, and its development must be fostered as one of the highest aims and objects of our science.

It cannot be desirable to leave the question on its present footing; and if we have any opportunity of bringing the existing doubts and misgivings to a distinct issue, it cannot be right to delay such a consummation.

Such are the feelings which induced me to accept the invitation with which the Council has honoured me, and to bring before you an analysis of the evidence of the present atomic theory, as I conceive it to exist dispersed in the minds and among the hands of chemists at the present time.

I propose to consider the subject under three successive headings.

1st. The proportions by weight in which elements replace one another, or their so-called equivalent weights, and the multiples of those proportions.

2nd. The units of chemical action, or the so-called molecules.

3rd. Atomic values.

Equivalent Weights.

Quantitative analyses have shown that the weight of oxygen which combines with one part by weight of hydrogen to form water, is eight times as great as that of the hydrogen; that the

weight of chlorine which combines with one part by weight of hydrogen to form hydric chloride is 35.5 times as great as that of the hydrogen. Whenever we displace oxygen from water by chlorine, forming hydric chloride, we find that for every eight parts by weight of oxygen so displaced, thirty-five and a half parts by weight of chlorine are taken up; and whenever we perform the opposite substitution, viz., displace chlorine from hydric chloride by oxygen so as to form water, we find the inverse ratio, viz., eight parts by weight of oxygen, replacing 35.5 parts by weight of chlorine. These numbers, 8 and 35.5, represent the relative weights in which oxygen and chlorine combine with the unit weight of hydrogen, and they are called the equivalent weights. The decomposition of ammonia by heat yields nitrogen gas and hydrogen in the proportion of $4\frac{2}{3}$ parts by weight of nitrogen to one of hydrogen, and in like manner the decomposition of marsh-gas yields three parts by weight of carbon to every one of hydrogen. Moreover, when we displace nitrogen from ammonia by chlorine, forming hydric chloride, we find that chlorine takes the place of the nitrogen in the proportion of 35.5 parts to $4\frac{2}{3}$; and in like manner when chlorine displaces carbon from marsh-gas forming hydric chloride, it does so in the proportion of 35.5 parts to 3 of carbon. So also when oxygen replaces carbon in marsh-gas forming water, we find that eight parts of oxygen take the place of three of carbon.

We have accordingly, from the comparison of these hydrogen compounds,—

35.5	as the equivalent weight of chlorine,		
8	"	"	oxygen,
$4\frac{2}{3}$	"	"	nitrogen,
3	"	"	carbon.

But chlorine can be made to replace the hydrogen in marsh-gas by successive steps, and we find that it does so in the proportion of 35.5 parts by weight to one part of hydrogen, and in the product so formed hydrogen can be made to replace chlorine, reproducing marsh-gas always in the proportion of one part by weight to 35.5 of chlorine.

Upon this and similar evidence we attribute to hydrogen, in relation to chlorine, the equivalent weight 35.5, and by so doing we extend our meaning of the word equivalent. 35.5 parts of chlorine are equivalent to 8 of oxygen, because they combine

with the unit weight of hydrogen; and 35.5 of chlorine are equivalent to one of hydrogen, because the elements replace one another in that proportion by weight in their compounds. In like manner oxygen can be made to replace hydrogen in ammonia and in marsh-gas, forming nitrous acid and carbonic acid respectively. It there reacts in the proportion of the same equivalent weight which it has in relation to chlorine. Nitrogen and carbon can, partly by such-like direct reactions, and partly by indirect reactions, be proved to replace hydrogen in the proportion of the same weights in which they combine with it. So that the equivalent weights of chlorine, oxygen, nitrogen, and carbon are the weights of those elements capable of combining (directly or indirectly) with the unit weight of hydrogen, or of replacing the unit weight of hydrogen.

Several other metals have been found to be analogous to hydrogen, viz., lithium, sodium, potassium, silver, &c., and to replace it in combination with chlorine or oxygen in the proportions corresponding to the following equivalent weights:—Lithium 7, sodium 23, potassium 39, silver 108, &c.; and in like manner bromine and iodine have been found analogous to chlorine, and to replace it in equivalent weights corresponding to 80 of bromine and 127 of iodine.

In the compounds ClH , ClK , BrH , BrK , ClAg , ICl , BrLi , OH_2 , OHK , ONa_2 , OClH , NH_3 , NH_2K , NK_3 , CH_4 , CH_3Cl , CH_2Cl_2 , CHCl_3 , CO_2 , the elements are contained in proportions corresponding to the equivalent weights above mentioned. But there are other compounds in which they occur in different proportions; thus iodine combines with chlorine in the proportion of 127 to 35.5, and also in the proportion of $42\frac{1}{3}$ to 35.5; nitrogen also combines with hydrogen and chlorine in the common compound, sal-ammoniac, and in the other compounds like it, in the proportion of $2\frac{1}{5}$ to every one of hydrogen or the equivalent weight of another element. Carbon combines with oxygen in a second proportion in carbonic oxide, viz., that of 3 to 4, and with hydrogen in many other proportions besides that which occurs in marsh-gas: viz., in methyl, four parts of carbon to one of hydrogen, in olefiant gas, six parts of carbon to one of hydrogen, and in acetylene, twelve parts of carbon to one of hydrogen, besides many others intermediate between these.

Now, Dalton knew the two oxygen-compounds of carbon, besides marsh-gas and olefiant gas. He represented the oxide

as containing one equivalent of oxygen weighing 8, with one of carbon weighing 6; the acid as containing twice 8 parts by weight of oxygen, combined with 6 of carbon.

In like manner, he considered olefiant gas as a compound of one equivalent of carbon, weighing 6, with the unit of hydrogen, marsh-gas as 6 of carbon with two units of hydrogen.

Some other compounds he found, partly by his own analyses, partly by analyses made by other chemists, to contain their elements in proportions approaching to simple multiples of certain weights peculiar to those elements respectively. He explained this coincidence by representing compounds as built up of atoms of their elements in various proportions to one another.

Many other elements are now known to combine in various proportions, which may be so represented, and it is common to refer to the fact which Dalton explained by atoms, as the law of multiple proportions.

It is desirable that we analyse the evidence which is now before chemists of these multiple proportions, and further their connection with the atomic theory.

The analyses known to Dalton have by the progress of chemistry been, for the most part, replaced by others more accurate and more trustworthy, and some of the numbers representing the combining proportions of elements, have undergone considerable modifications in consequence of our improved methods of observation; but both Dalton and we agree in one respect, viz., that taking the best numbers we can get by analyses, we calculate the composition of every compound, on the assumption that it must be built up of integral multiples of certain numbers belonging to the elements respectively; and it must be admitted as a *primâ facie* confirmation of the justice of this assumption, that the more perfect our methods of observation become, and the more carefully they are applied, the more nearly do our experimental results agree with multiple proportions of such numbers.

In the case of compounds of very simple constitution, the agreement between our experimental results and the theory of multiple proportions is so close, that it would be unreasonable to attribute the coincidences to chance. But, on the other hand, the progress of research leads frequently to the discovery of compounds of which the constituents are present in less simple

proportions, and others again in which the proportion can be represented only by high numbers. And in many cases the difference between the numbers corresponding to the formula which is admitted, and the numbers corresponding to some other formula, is not greater than the unavoidable errors of experiment. So that analysis does not decide which of the formulæ is the true one, nor does it furnish an argument in favour of any formula. Thus a high term of the marsh-gas series, such as $C_{27}H_{56}$, cannot be analysed with certainty. The numbers found by combustion were—

C 85.5

H 14.9.

The formula $C_{27}H_{56}$ requires C 85.27 H 14.73,		the formula $C_{26}H_{54}$ requires C 85.25 H 14.75.		and $C_{27}H_{54}$ requires C 85.71 H 14.29
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The actual result of observation agrees with none of these formulæ, yet, in examining it, chemists assume that it ought to agree with some such formula. They select the most probable, and attribute to errors of observation the divergence from it.

The most important evidence brought to bear on the composition of this body was of two kinds: first, an examination of a silver-salt, formed from the product of its cautious oxidation, and containing the following percentages, viz. :—

C 62.36

H 10.31

Ag 20.92,

which approach more nearly to the numbers—

C 62.66

H 10.25

Ag 20.9,

required by the formula $C_{27}H_{53}AgO_2$, than to any other probable formula; and, secondly, a study of the action of bromine upon it proving that it was a marsh-gas and not an olefiant gas, like that last mentioned.

The hydrocarbon itself approached nearer in composition to the formula $C_{27}H_{56}$ than to any other, and the study of two of its reactions thus agrees in indicating that formula for the original hydrocarbon as more probable than any other atomic formula.

It would be quite correct to say that *some* elements are found capable of uniting with one another in the proportion of simple multiples of certain weights, and not in intermediate proportions. Thus carbon unites with oxygen in the proportion of 12 parts of carbon to 16 of oxygen, and also in the proportion of 12 of carbon to 2×16 of oxygen. If we take less oxygen than 16 parts to every 12 of carbon, some of the carbon remains as such uncombined, and no compound of the two elements has ever been got with less oxygen than 16 parts to every 12 of carbon. But if we take more and more oxygen in proportion, we find that carbon can unite with it till it has got 2×16 parts. Yet we do not admit that it unites in all proportions intermediate between 16 and 2×16 , for by examining these products, formed by adding more and more oxygen to the compounds of 16 grammes with 12 carbon, we find that they are mixtures of carbonic acid and carbonic oxide; the former being rapidly soluble in aqueous potash, whereas the latter remains undissolved.

But the theory of multiple proportions is not limited in so modest a manner. It is applied to all elements and to all compounds of them, in spite of the fact that the usual results of observation require straining to agree with any multiple formula, and the immense majority of substances have not as yet been reduced by the process to any definite formulæ whatever. The very great majority of mineral and of organic substances which we meet with on the surface of the earth, have not been proved to have a composition agreeing with any formula.

When multiple proportions are spoken of, it is not usually explained whether multiples of equivalent weights are meant, or multiples of the atomic weights of the elements. It is sometimes asserted that we have a law of multiple proportions, which is a direct representation of experimental facts, whereas the atomic theory is a hypothesis, and independent of such law. Those who make this statement must be understood to refer to multiples of equivalent weights, and not to multiples of atomic weights; for if, as they assert, atomic weights are hypothetical, then any relation between the multiples of atomic weights are only multiples of hypothetical numbers, and cannot have greater certainty than the atomic weights themselves.

If we knew the empirical proportions of elements, and did

not believe in atoms, we should describe carbonic oxide as the compound of three parts of carbon with four of oxygen, and carbonic acid as the compound of three parts, by weight, of carbon with eight of oxygen. The hydrocarbons mentioned would be described as follows, viz.: marsh-gas, as a compound of three parts of carbon with one of hydrogen; olefiant gas, a compound of six parts of carbon with one of hydrogen; methyl, a compound of four parts of carbon with one of hydrogen; ethyl, a compound of twenty-four parts of carbon with five of hydrogen; and so on. We should probably use the simplest entire numbers corresponding to the actual proportion between the elements; but we should not use the higher numbers standing to one another in the same proportions which are introduced by the atomic theory.

It is quite true that the elements of some simple, well-known compounds are shown by analysis to be present in proportions corresponding to simple multiples of a particular weight belonging to each of them respectively; but in compounds of less simple constitution, no such relation is obvious. The analysis of most organic bodies does not suggest any simple proportion between the numbers of those weights of their constituents, and it sometimes suggests a relation which is not the true one. Thus, the only simple representation of the results of analyses of the high term of the marsh-gas series above mentioned, would be to describe it as containing six parts, by weight, of carbon to one of hydrogen. The actual process by which we establish the composition of such complex bodies is by *assuming* that the composition of each of them must correspond to entire multiples of the atomic weights of their elements, and by treating as errors of observation any divergence between the proportions discovered by analysis and such atomic proportions.

It is not easy to judge of the evidence of one part of a system by itself. The doctrines of equivalence, of molecular weights, and of atoms mutually support one another, and are habitually used by chemists in connection with one another. Our present task is to examine the doctrine of multiple proportions of equivalents; first, in respect of the evidence upon which it rests; secondly, in respect of the proof which it affords, if any, of the existence of atoms.

The second question may be best investigated in the form of a comparison between the atomic method of multiples, and

what I may be permitted to call the tomic method of sub-multiples; carbonic acid is represented in the atomic plan as containing twice as much oxygen as is contained in carbonic oxide; whereas, on the other plan, it may be represented as differing from carbonic oxide by containing half as much carbon as is contained in the oxide. It is true that by combining oxygen with carbonic oxide we get carbonic acid; but it is equally true that by combining carbon with carbonic acid we obtain carbonic oxide. As far as the proportion of the elements is concerned, we have no better right to suppose that the carbon is indivisible, and that the acid contains twice as much oxygen as the oxide, than we have to suppose that the carbon is divisible, and that half of the carbon is taken out of carbonic oxide in forming carbonic acid.

We cannot be too careful in considering this fact, for many important consequences follow from it. Our proposition relates to an undefined quantity of carbonic oxide. It is known that by combining four parts, by weight, of oxygen with seven parts by weight of carbonic oxide, we get exactly eleven parts of carbonic acid; or, what is the same thing from another point of view, that if we take away four parts of oxygen from eleven of carbonic acid, we get seven of carbonic oxide. It is also known that if we take away 1.5 parts of carbon from 7 of carbonic oxide, we get 5.5 parts of carbonic acid; and, reciprocally, that if we add 1.5 parts of carbon to 5.5 of carbonic acid, we get 7 of carbonic oxide. These parts by weight may be tons, or pounds, or ounces, or grains, or any other actual experimental weight. A philosopher disbelieving in the existence of atoms, would point out that whereas the divisibility of matter is infinite, we find that by the chemical processes available for the removal of carbon from carbonic oxide, the carbon divides into equal portions, one remaining with the oxygen, the other leaving it; and his statement that this half of the carbon is added on again when the process is reversed, is as consistent with the evidence as that of the believer in atoms, who asserts that in forming carbonic acid, oxygen is added in quantity equal to the oxygen in the carbonic oxide, while the formation of carbonic oxide from the acid consists in taking away half the oxygen. What has been here said of the proportions between the elements in carbonic oxide and carbonic acid may be said with equal force

of the proportions between the elements contained in other compounds, such as the following:—

$\text{FeCl}_2, \text{FeCl}_3, \text{CH}_4, \text{CH}_3, \text{CH}_2, \text{C}_2\text{H}_3, \text{CH}, \text{NH}_3, \text{NH}_4\text{Cl}, \text{SH}_2, \text{SCl},$
 $\text{OH}_2, \text{OH}, \text{PI}_2, \text{PCl}_3, \text{PCl}_5, \text{ICl}, \text{ICl}_3, \text{SiCl}_4, \text{SiF}_6\text{K}_2, \text{PtCl}_2,$
 $\text{PtCl}_4, \text{PtCl}_6\text{K}_2, \text{BF}_3, \text{BF}_4\text{K}, \text{AuCl}, \text{AuCl}_3, \text{AuCl}_4\text{Na}, \text{CrCl}_2, \text{CrCl}_3,$
 $\text{CrF}_6, \text{SnCl}_2, \text{SnCl}_4, \text{HgCl}, \text{HgCl}_2, \text{CuI}, \text{CuCl}_2.$

If we examine consistently with the principles above adopted, the equivalent weight of each element contained in these compounds, we find that we must describe it as the weight which in any compound is combined with the unit of hydrogen, or might be replaced by it. This is easily obtained by dividing the number represented by the atomic symbol by the number of equivalents of the hydrogen or chlorine families with which it is combined.

We thus obtain the values :

$\frac{\text{Fe}}{2}, \frac{\text{Fe}}{3}, \frac{\text{C}}{4}, \frac{\text{C}}{3}, \frac{\text{C}}{2}, \frac{2\text{C}}{3}, \text{C}, \frac{\text{N}}{3}, \frac{\text{N}}{5}, \frac{\text{S}}{2}, \text{S}, \frac{\text{O}}{2}, \text{O}, \frac{\text{P}}{2}, \frac{\text{P}}{3}, \frac{\text{P}}{5}, \text{I}, \frac{\text{I}}{3}, \frac{\text{Si}}{4},$
 $\frac{\text{Si}}{8}, \frac{\text{Pt}}{2}, \frac{\text{Pt}}{4}, \frac{\text{Pt}}{8}, \frac{\text{B}}{3}, \frac{\text{B}}{5}, \text{Au}, \frac{\text{Au}}{3}, \frac{\text{Au}}{5}, \frac{\text{Cr}}{2}, \frac{\text{Cr}}{3}, \frac{\text{Cr}}{6}, \frac{\text{Sn}}{2}, \frac{\text{Sn}}{4}, \text{Hg},$
 $\frac{\text{Hg}}{2}, \text{Cu}, \frac{\text{Cu}}{2}.$

I have taken only a few of the well known compounds, yet among them there are ten elements, each of which has two distinct equivalent weights, four of the elements have got three equivalent weights each, and another (carbon) is shown to have five different equivalent weights. It might easily be shown to have many more.

Now it is interesting to observe that whenever examples are given of the supposed law of multiple proportions, Chemists take not these fractional expressions representing equivalents, but usually the atomic symbols themselves. They describe, in fact, *atoms* as occurring thus combined with one another in the proportions of entire multiples of their weight; in fact, the so-called law of multiple proportions has no existence apart from the atomic theory; those who adopt it seem not to be aware that they are using the notion of atoms, or else they are shy of mentioning it.

The fact that two elements, such as carbon and oxygen, are

capable of combining in more than one proportion is in reality (when we consider it by itself) quite as much an argument against the atomic theory as an argument in favour of it. That the carbon in carbonic oxide can be divided in the proportion of $\frac{1}{2}$, or the oxygen can be multiplied in the proportion of 2 to 1, are equally true statements of the proportion. If oxygen could neither take more nor less carbon than in the proportion of three parts by weight to every four of oxygen, we could say with certainty that that proportional weight of carbon cannot be divided, or in other words that it is an atomic proportion; but the existence of the two compounds, although not inconsistent with the atomic theory, points as much to proportional divisibility of carbon as to proportional multiplicability of oxygen.

When one of those who profess to disbelieve in the atomic theory has ascertained by analysis the percentage composition of a compound, and wants to find its formula, he divides the percentage weight of each element by its atomic weight. He seeks for the smallest integral numbers which represent the proportion of atoms, and he attributes to impurity of his sample or to errors of analysis any deviation from the atomic formula thus obtained. He looks to the reactions of the body for aid in constructing his atomic formula, and controls his analyses by considerations derived from well established reactions, but whenever he is led by any of these considerations to a formula which contains a fraction of any atomic weight, he takes a multiple of the formula sufficiently high to be entirely free from such fractions. In no case does he reason on a basis independent of the atomic theory.

Existence of Molecules.

The atomic theory led to the discovery of molecules. Chemists saw in the phenomena of combination in multiple proportions, processes which were in accordance with their pre-conceived belief in atoms, and they studied combining proportions from the point of view of atoms. They acted on the assumption that each element consists of small indivisible particles of like nature; that the atoms of each element are different in many chemical properties, and usually in weight, from those of every other element; that the unlike atoms combine

together in various relative numbers to form clusters, or so-called molecules, every pure compound consisting of such molecules, each one like the rest, but differing from the molecules of every other compound. Thus a given quantity of carbonic oxide was supposed to consist of an aggregate of molecules, each one composed of an atom of carbon united with an atom of oxygen; carbonic acid, to consist of molecules, each one built up of three atoms, viz., one of carbon, and two of oxygen. In calculating the molecular weight of any compound from the ascertained proportion of its elements, they assumed that each molecule must contain at least such a number of atoms of each of its elements as would, when multiplied by the atomic weight of the respective elements, represent the actual proportion by weight in which the elements had combined. Thus 44 parts by weight of carbonic acid have been found to contain 32 of oxygen, and twelve of carbon. Two atoms of oxygen, each weighing 16, with one atom of carbon weighing 12, must be contained in the smallest existing particle of carbonic acid.

Ammonia contains hydrogen and nitrogen in the proportion of 3 parts of the former to 14 of the latter. 3 atoms of hydrogen, each weighing 1, with one atom of nitrogen weighing 14, represent the simplest molecular constitution corresponding to that proportion of the elements. The molecule of olefiant gas, in like manner, must contain at least one atom of carbon with two atoms of hydrogen, while that of marsh gas contains at least one of carbon with four of hydrogen.

An acid hydric salt, the tartrate, was found by analysis to contain carbon, hydrogen, and oxygen, in proportions corresponding to the minimum formula $C_2H_3O_3$. When neutralised by potash, its solution yielded a potash salt corresponding to the minimum formula $KC_2H_2O_3$, and it is known that the weight of hydric sulphate indicated by the formula $\frac{SO_4H_2}{2}$ or $\frac{S}{2}O_2H$ would react on the same weight of potash forming a neutral salt. This relation between the tartrate and sulphate may be expressed by saying that 75 parts by weight of the tartrate are equivalent to 49 parts by weight of the sulphate.

In like manner a compound of basic properties, called quinia, was found to contain carbon, hydrogen, nitrogen, and oxygen, in proportions which can be represented by the minimum formula $C_{10}H_{12}NO$. It was found that the base unites with hydric

chloride, and forms a platinum-salt, analogous to the salt formed by ammonia, and known to have the composition $\text{PtCl}_6\text{H}_2(\text{NH}_3)_2$. The weights of these bases denoted by the formulæ NH_3 and $\text{C}_{10}\text{H}_{12}\text{NO}$, are accordingly equivalent to one another in the sense in which we have hitherto used that word. It is well known that, in the actual development of our knowledge of these relations, the notion of equivalence sprang up among acids and bases, and was extended from them to elementary bodies.

It is interesting and instructive to observe, that, for a considerable time, the proportions in which compounds react on one another were represented by formulæ according to the atomic theory as it then prevailed, which recorded the empirical proportions of the constituents, but were not correct or consistent representations of the molecular weights. These labours served to collect an immense amount of evidence for the establishment of molecular weights, but the end was not distinctly in view, and the only rational guide was the imperfect atomic theory then existing.

Thus the great Berzelius, the master spirit of that period, used formulæ which in our system of atomic weights may be thus rendered:

Water	H_2O
Potash	K_2O
Potassic hydrate	$\text{H}_2\text{OK}_2\text{O}$
Nitric acid.....	N_2O_5
Potassic nitrate	$\text{K}_2\text{ON}_2\text{O}_5$
Hydro-potassic sulphate	$\text{H}_2\text{OSO}_3\text{K}_2\text{OSO}_3$
Ether.....	$\text{C}_4\text{H}_{10}\text{O}$
Alcohol	$\text{C}_4\text{H}_{10}\text{OH}_2\text{O}$
Carbonic acid	CO_2
Carbonic chloride.....	CCl_4
Phosgene	CO_2CCl_4
Chloro-sulphuric acid	$2\text{SO}_3 + \text{SCl}_6$
Chloro-chromic acid.....	$2\text{CrO}_3 + \text{CrCl}_6$
Bismuthic oxychloride.....	$\text{Br}_2\text{O}_3\text{BrCl}_3$
Hydric chlor-acetate ($\text{C}_2\text{Cl}_3\text{HO}_2$)..	$\text{C}_2\text{O}_3\text{C}_2\text{Cl}_6\text{H}_2\text{O}$
Hydric oxamate ($\text{C}_2\text{NH}_3\text{O}_3$)	$\text{C}_2\text{O}_3\text{H}_2\text{OC}_2\text{O}_2\text{N}_2\text{H}_4$
Bichlorinated ether ($\text{C}_2\text{H}_3\text{Cl}_2$) $_2\text{O}$..	$2\text{C}_4\text{H}_6\text{Cl}_6\text{C}_4\text{H}_6\text{O}_3$.

Some of his atomic weights were inconsistent with our mole-

cular formulæ. Thus hydrogen, chlorine, nitrogen, and some other elements, he really treated as having atomic weights twice as great in relation to oxygen as we now consider them to have. For his couple of volumes of hydrogen, denoted by the symbol H , were not allowed to separate from one another, so that his formula HO for water was in its uses similar to the formula HO , and analogous to his formula for potash, which was written KO .

The theory of radicals did much towards classifying compounds. The names ammonium and cyanogen were given to groups of elements which exhibited analogies with single elements. Ethyl was another radical which did admirable service; and benzoyl afforded an instance of a radical of another kind.

The theory of organic radicals is in reality an extension of the atomic theory, and it was needed as a step towards the proof of that theory.

The equivalent proportions of elements, and the multiples of those proportions in which they combine, afforded no proof of the existence of atoms, but they led to the discovery of compound atoms analogous to undecomposed atoms. At the same time, many of these organic radicals, although exhibiting the closest analogy with elements, are known to be only capable of existing under certain conditions, and are easily burnt or decomposed.

It was a great step to extend the use of the word atom to groups of elements known to hold together only under certain limited conditions. For by including in one common term, atom, the smallest particles of the elements, and the smallest particles of these compounds which behave like elements, we deprive the word atom of the only objectionable peculiarity of which it might have been accused. It is no longer an absolute term; and in its application to the elements it denotes the fact that they do not undergo decomposition under any conditions known to us. If anybody use the word in its absolute sense in its present applications, he is guilty of a manifest inconsistency.

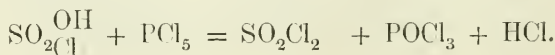
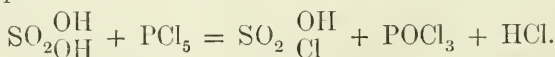
It must not, however, be supposed that the existence of groups of elements, which perform functions analogous to those of single elements, is any proof of the existence of atoms, for compounds like $\text{C}_2\text{H}_5\text{Cl}$, $\text{C}_{16}\text{H}_{33}\text{Cl}$, NH_4Cl , $\text{C}_6\text{H}_7\text{Cl}$, &c., may be

represented as containing submultiples of the less numerous atoms, just as NH_3 can be represented as $\frac{N}{3}\text{H}$, or CO_2 as $\frac{\text{C}}{2}\text{O}$.

One of the most fruitful ideas in the work of establishing the molecular constitution of compounds, was the idea of types—and the correlative idea of substitution. If we maintain unity of type, the knowledge of a few molecular formulæ serves as a guide to many others. Thus, if we take water as H_2O , alcohol can be proved by normal substitutions to be $\text{C}_2\text{H}_6\text{O}$. We find that phosgene reacts upon alcohol according to the equation $\text{C}_2\text{H}_5\text{OH} + \text{COCl}_2 = \text{C}_2\text{H}_5\text{OCOCl} + \text{HCl}$, whereas, if the molecular formula of Berzelius for phosgene were true, the first action would be $\text{C}_2\text{H}_6\text{O} + \text{C}_2\text{O}_2\text{Cl}_4 = \text{C}_2\text{H}_5\text{OC}_2\text{O}_2\text{Cl}_3 + \text{HCl}$; the second action would be the formation of the compound $\text{C}_2\text{O}_2\text{Cl}_2\text{O}_2(\text{C}_2\text{H}_5)_2$.

The process is a mere replacement of chlorine by $\text{C}_2\text{H}_5\text{O}$, forming a compound of the molecular formula $\text{C}_3\text{H}_5\text{ClO}_2$, instead of one of double that formula. Now, having found that as small a weight as COCl_2 can take part in one distinct reaction, we know that the molecular weight is not greater than that. Again, the molecular formula of water being known, we have the reaction $\text{SO}_2\text{Cl}_2 + \text{H}_2\text{O} = \text{SO}_3\text{HCl} + \text{HCl}$, and $\text{SO}_3\text{HCl} + \text{H}_2\text{O} = \text{SO}_4\text{H}_2 + \text{HCl}$, which establish for chlorosulphuric acid the maximum formula SO_2Cl_2 , and for hydric sulphate the formula SO_4H_2 . So also the hydric chloracetate reacts on a molecule of potassic hydrate thus, $\text{C}_2\text{HCl}_3\text{O}_2 + \text{HOK} = \text{C}_2\text{KCl}_3\text{O}_2 + \text{H}_2\text{O}$. In these reactions there are alternative explanations: thus, if phosgene is $\text{C}_2\text{O}_2\text{Cl}_4$, then the ether $\text{C}_3\text{H}_5\text{ClO}_2$ must have double that molecular weight: for the reaction is a regular double decomposition, in which no indication of increase or diminution in the number of molecules takes place.

With the chloro-sulphuric acid there is a similar alternative. $\text{S}_3\text{O}_{12}\text{H}_6$ must be the molecular formula of hydric sulphate, if $\text{S}_3\text{O}_6\text{Cl}_6$ be that of the chloro-acid: for the above reaction is as normal as possible, and, moreover, we can recover the chloro-acid from the hydric salt by a couple of steps as normal, as far as the sulphate is concerned:—



In order to judge of the evidence of molecular weights obtained by a study of chemical reactions, we ought to consider, on the one hand, what properties must belong to compounds built up of atoms, and, on the other hand, what properties might belong to them if there were no limit to the divisibility of each kind of elementary matter.

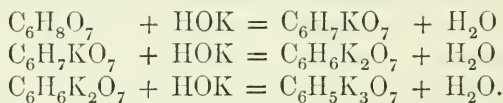
Now the first and most essential characteristic of every molecule is that it possesses a weight equal at least to the sum of the atomic weights of its constituents, in such number as represents the simplest proportion consistent with a correct analysis. Thus a compound containing iron and oxygen in such proportions by weight as correspond to three atoms of oxygen to every two atoms of iron, must have at least as great a molecular weight as $2 \times 55 + 3 \times 16$. On the other hand, if iron and oxygen, when combined in this proportion, were infinitely divisible, one would be able to get smaller weights of the oxide to take part in reactions, than such as are 160 times as heavy as the unit weight of hydrogen. We can replace the oxygen in this oxide by chlorine; we can combine it more or less fully with sulphuric acid, or with other acids; we can decompose these salts by other compounds; we can combine them with other salts; and we can compare each of these products with the original oxide, quantifying the proportions of the materials which take part in each transformation: and the result of it all is that we get a chain of evidence proving that less than 160 parts of ferric oxide never take part in any reaction.

So again with other bodies.

Thus a base composed of carbon, hydrogen, and nitrogen was obtained, which could not be represented by a simpler formula than $C_6H_{15}N$. The atomic theory tells us that less than $72 + 15 + 14 = 101$ parts by weight of this base cannot possibly take part in any reaction. We bring it in contact with hydric chloride in varying proportions, beginning with very little of the chloride. By examining the product, we find it is a mixture of the unchanged base with a compound containing carbon, hydrogen, nitrogen, and chlorine, in proportions corresponding to the formula $C_6H_{16}NCl$, and containing exactly 101 parts of the base with one part by weight of additional hydrogen and 35.5 parts of chlorine. If we add our hydric chloride to the base, exactly in this proportion, we have nothing left of either material uncombined with the other; and if we add more hydric

chloride, such excess is left uncombined and unchanged. The base does react on hydric chloride in the proportions indicated by its atomic formula, and has not been found to react in any other proportion.

Take an acid salt like hydric citrate, $C_6H_8O_7$ being the simplest atomic formula representing its composition. By bringing it in various proportions in contact with a solution of potassic hydrate, we find that it is capable of reacting in three distinct proportions on that basic hydrate—



If we look through the reactions of well-known bodies with one another, we find that there are many which are not made out quantitatively; but not one of the enormous number that we know accurately and with certainty, has shown a combining proportion of molecules at variance with the atomic theory, and corresponding to the idea that matter is infinitely divisible.

The density of gases and vapours has afforded valuable independent confirmation of the truth of the atomic constitution of molecules, for every compound which evaporates without decomposition has a vapour-density proportional to its molecular weight.

The great benefits conferred upon our science by the doctrine of types would have been impossible without the doctrine of radicals. The two theories were for a considerable time held by different chemists, and were supposed to be inconsistent with one another. They have proved to be essential to one another; so that it may confidently be asserted that those who showed that NH_4 may replace an atom of hydrogen, of potassium, &c., and that C_2H_5 may also perform such functions, prepared the way for the comparisons of bodies of one type.

Another class of considerations which have done admirable work in establishing molecular weights, are those relating to the number of products of substitution obtainable by altering the proportion of materials.

Thus hydric sulphate not only forms the neutral potassic sulphate which we considered in relation to the neutral tartrate,

but it also forms a double salt containing hydrogen and potassium, according to the formula HKSO_4 , when it is brought in contact with half or less than half as much potassic hydrate as is needed to form the neutral salt; and the fact that the hydrogen in the sulphate can be replaced by potassium, in the proportion of half or all, gives an independent proof that the minimum formula of the hydric salt must be $\text{H}_2\text{S}\text{O}_4$. So also the hydric tartrate forms, not only the neutral salt above mentioned, but also an acid double salt of hydrogen and potassium, for which the simplest formula is $\text{C}_4\text{H}_5\text{K}\text{O}_6$, and a double salt with sodium and potassium $\text{C}_4\text{H}_4\text{NaK}\text{O}_6$.

The common phosphates were proved by such evidence as this to be tribasic, and the oxalates, in like manner, to be bibasic. Other reactions confirm the conclusions thus arrived at. For instance, the bibasic salts yield two classes of amides—normal amides, such as oxamide $\text{C}_2\text{O}_2\text{N}_2\text{H}_4$, and compounds of amide and salt, like potassic oxamate $\text{C}_2\text{O}_2\text{OK}^{\text{NH}_2}$; and monobasic salts are distinguished from these not only by their inability to react in more than one proportion on potash or soda, but also by their inability to form compounds of amide and salt, like the oxamate. Again, bibasic hydrogen salts lose their water by heat, and monobasic hydrogen salts do not.

The classification of compounds by their analogies has been one of the most important operations for enabling us to see their distinctive resemblances and differences, and the establishment of series of homologous organic compounds has been, perhaps, the most perfect and useful case of such classification, as well as one of the most fruitful of benefit to the progress of science.

So well did the analogies and reactions among organic compounds serve to connect them with one another, by simple and natural principles, that the simpler part of the science has gained chiefly of late years by adopting methods and conclusions established in the more varied field of organic compounds. Thus, the chief arguments adduced by Gerhardt for the molecular weight of carbonic acid which we now adopt, and for the corresponding molecular weight of water, were to the effect that in no reaction between well known molecules is a smaller proportion of carbonic acid given off or taken up than that corresponding to the molecular weight 44; and, in like manner, less

than 18 parts, by weight, of water are never taken up nor given off in any well known reaction between molecules of known weight. The examples of molecules in each case were mainly taken from organic chemistry. The molecular weights of the gaseous elements, hydrogen, chlorine, nitrogen, oxygen, &c., were studied in great part with the aid of the light obtained from the comparison of organic reactions, in which they take part, especially the double decompositions which take place when chlorine normally replaces hydrogen.

A study of the phenomena of electrolysis, and some other inorganic processes, had led to metals being considered as possessing, in the free state, a molecular constitution analogous to that of compounds; and Brodie's reduction of oxides by oxygen gave evidence of combinations between atoms of oxygen in forming the free gas.

Amongst the general processes which were instrumental in judging of the correctness of molecular formulæ was Gerhardt's so-called law of even numbers. Among molecular formulæ which he considered well established, he observed that the sum of the atoms of a certain list which he supplied was always an even number; whereas, the sum of the atoms of elements not belonging to his list was sometimes an even, sometimes an uneven number.

The circumstance is now known to be one among several consequences of a difference in replacing value, which constitutes one of the most important characteristics of atoms, and we also know that many elements which Gerhardt classed with hydrogen, nitrogen, &c., do not belong to that class; but even in its original imperfect form the rule rendered very important services. Thus, such formulæ as $C_2H_3O_3$, $C_{10}H_{12}NO$, Gerhardt knew could not be molecular formulæ, and must be at least doubled. A study of their reactions amply confirms his verdict. We also know that such formulæ as $FeCl_3$, $HgCl$, $AlCl_3$, cannot represent molecules, and must be corrected so as to contain at least even numbers of chlorine atoms without including the metallic atoms in the account.

To do justice to the completeness of the evidence which is obtained respecting many molecular weights, by these purely chemical methods of research, it would be necessary to go into the full particulars of the operations and observations in the respective cases, and that would task, still more unduly than I

am now tasking it, the indulgence of the Society. But I feel convinced that the brief indications which I am able to give of the kind of evidence obtained under these various headings, will recall to the minds of chemists the particulars which it would be needful to describe specially to persons not intimately acquainted with the science.

There are, however, other properties of molecules which have been noticed since chemists discovered the existence of the molecules themselves, and these are of kinds to be more easily understood by all—properties which involve no change of composition in the molecules, but which belong to them as long as they subsist.

Of these physical properties, one of the most important is the volume of molecules in the state of gas or vapour. Whenever we examine perfect vapours composed of like molecules, we find that whatever the molecules may be, they occupy the same volume under like conditions. In other words, these little units of matter, found by the guiding aid of the atomic theory, are found also to be units of force when examined under those conditions. There have, in several cases, been important discrepancies between the chemical evidence of molecular constitution and the evidence afforded by vapour-volume. Thus, hydric sulphate and ammoniac chloride are among the compounds of whose molecular weights we have the best and most varied chemical evidence, yet the vapour formed from each of these occupies about double the volume of a gas molecule. A careful examination of the vapour formed from each of them showed, however, that it is a mixture of molecules of two sorts formed by the decomposition of the original compound. The fact that errors in the indications supplied by vapour-density could be thus pointed out by the chemical evidence of molecular weight is surely no slight confirmation of the perfection of the evidence of molecular weights obtainable by chemical methods; and, on the other hand, the immense number of coincidences between the indications obtained from the two independent sources is a strong evidence of the truth and parallelism of the two.

There are, also, crystalline compounds, which chemistry has found to be closely analogous, which occupy, in the crystalline state, equal, or nearly equal, volumes.

Among other physical properties which confirm the truth of

the atomic views of molecular constitution are boiling points. Whenever truly analogous elements are comparable in respect to boiling points, it is found that those composed of heavier atoms boil at higher temperatures than those composed of lighter atoms. A comparison of the successive terms of the series—chlorine, bromine, and iodine, illustrates this difference very strikingly. So also a comparison of the several terms of the series—oxygen, sulphur, selenium, and tellurium, and not less so the elements nitrogen, phosphorus, arsenic, antimony, and bismuth.

Now, whenever volatile organic compounds belonging to a homologous series are compared, it is found that of two such compounds, the one having the higher molecular weight has also the higher boiling point. The glycols present, however, an exception to this general observation.

The melting points of homologous organic compounds also show differences running parallel in like manner to their differences of molecular weight.

The relative velocities of motion of particles, as shown by the processes of diffusion, afford another confirmation of the general truth of the molecular weights; for, on the one hand, it is known that heavy particles diffuse more slowly than light particles; on the other hand, a comparison of the relative velocities of movement of molecules of relative weights, previously determined upon chemical evidence, shows that the heavier molecule of chemistry is also the heavier molecule in diffusion.

At this point of my study of this question I am in a serious difficulty, for molecules have no *locus standi* in the absence of the atomic theory. They are, to use the words of Dumas, physical atoms; their existence is a necessary consequence of the atomic theory, and all chemical reactions agree in proving their existence. They are also discovered by an examination of the mechanical properties of gases.

The opponents of the atomic theory are bound to explain, in some other way, the facts which point so distinctly to the existence of molecules, if they wish to advance from the position of mere contradictors to that of chemists.

Hitherto they have not done so, and the case stands thus: on the one hand, we have a simple theory which explains in a consistent manner the most general results of accurate observation in chemistry, and is daily being extended and

consolidated by the discovery of new facts which range themselves naturally under it. On the other hand, we have a mere negation: for the statements of those who say that our evidence of the existence of atoms is not conclusive, and yet omit to show any alternative theory, are nothing more. In discussing the relative composition of carbonic acid and carbonic oxide, I have endeavoured to put the negation in a tangible form, as an affirmation that there are no limits to the divisibility of elements, and to represent compounds containing multiples of equivalent weights as containing sub-multiples corresponding to the same empirical proportions.

If elements, in combining with one another, merely undergo more minute subdivision, so that a compound, like amylic alcohol, $\text{CH}_{1\frac{2}{3}}\text{O}_{\frac{1}{3}}$, is formed from methylic alcohol by removing hydrogen and oxygen from the compound CH_4O , then we could expect a weight of it corresponding to a formula containing less hydrogen and oxygen to perform the functions of the molecule CH_4O .

Of two things, one: either the existence of molecules is denied, or it is admitted.

In the former case, the vast and consistent body of chemical evidence of the existence of molecules must be set aside and disproved, and the physical confirmations of their existence must also be proved to be erroneous.

In the latter case it must be shown by quantitative analysis that those complex molecules to which we attribute a great weight, are really lighter than their simpler analogues.

Now, the difficulty is to choose arguments for an opponent. It would probably matter little to us which they might select; but when they content themselves with saying that we are wrong, without either showing in what respect our evidence or our reasonings are at fault, and without showing any other evidence or any other reasonings which they consider preferable, it is difficult to know what else to do with them than to state our case and leave them to their reflections.

Atomic Values.

The most important and weighty chemical property of atoms as yet discovered, is one which can only be perceived by the aid of a knowledge of the equivalent weights of the elements and of the molecular weight of a considerable number of compounds.

Thus if we know the molecular formulæ of the following compounds, we can compare them with one another and perceive their differences of composition :

Hydric acetate has the molecular formula	$C_2H_4O_2$
Hydric monochloracetate	$C_2H_3ClO_2$
„ dichloracetate	$C_2H_2Cl_2O_2$
„ trichloracetate	$C_2HCl_3O_2$
Again,	
Marsh-gas has the molecular formula....	CH_4
Methylic chloride	CH_3Cl
Methylenic chloride	CH_2Cl_2
Chloroform	$CHCl_3$
Carbonic chloride	CCl_4

It is apparent from these series of formulæ that one equivalent weight of chlorine can take the place of one of hydrogen in a molecule, or two of chlorine can replace two of hydrogen, or three replace three, and so on. Hydrogen-compounds containing in each molecule a much greater number of hydrogen equivalents, have been found to allow, in like manner, the hydrogen to be replaced, one equivalent at a time, by chlorine, and to the extent of a great number of equivalents in each molecule.

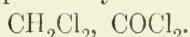
In like manner, potassium replaces hydrogen in molecules, sometimes in the proportion of an even number of equivalents, sometimes in the proportion of an uneven number of equivalents, as will be seen by the following molecular formulæ:—

H_2O	H_2SO_4	H_3PO_4	H_3N	$H_2C_4H_4O_6$
HKO	$HKSO_4$	H_2KPO_4	KH_2N	$HKC_4H_4O_6$
K_2O	K_2SO_4	HK_2PO_4		$K_2C_4H_4O_6$
		K_3PO_4		

When, however, oxygen takes the place of hydrogen, without change of equivalent weight, it is only in the proportion of two equivalents of oxygen replacing two of hydrogen, four of oxygen replacing four of hydrogen, six replacing six, and so on; always an even number of hydrogen equivalents replaced in each reaction of the kind. Thus carbonic acid is formed from marsh-gas by the normal reaction $CH_4 + 2O_2 = CO_2 + 2H_2O$, in which four equivalent weights of oxygen replace four of hydrogen. Hydric nitrate has a constitution similar to ammoniac hydrate, the difference being that it contains four equivalent

weights of oxygen instead of four equivalent weights of hydrogen in the ammonia, as will be easily seen by a comparison of the formulæ HONH_4 and HONO_2 .

Again, phosgene is methylenic chloride in which two equivalents of hydrogen are replaced by two of oxygen—



The compounds .. ammonia	$2\text{H}_3\text{N}$
nitrous acid.....	O_3N_2
glycoll.....	$\text{C}_2\text{H}_6\text{O}_2$
hydric glycollate	$\text{C}_2\text{H}_4\text{O}_3$
hydric oxalate.....	$\text{C}_2\text{H}_2\text{O}_4$

show a replacement of hydrogen by oxygen in steps, each one being two hydrogen replaced by two of oxygen. Now, it is not the existence of these compounds which proves any different value in oxygen atoms from chlorine atoms; it is the fact that no case is known of a molecule containing a single equivalent of oxygen in place of one of hydrogen, nor of three equivalents of oxygen in place of three of hydrogen, nor, in short, of any uneven number of hydrogen equivalents replaced by an uneven number of oxygen equivalents.

The same difference between oxygen and chlorine may be seen by comparing all well known molecular formulæ containing either one of those elements, apart from the particular process by which they may have been formed. Thus we have, by way of illustration, some bodies taken at random from various classes of compounds—

$\text{C}_2\text{H}_5\text{Cl}$	H_2O
$\text{C}_2\text{H}_4\text{Cl}_2$	CO
$\text{C}_2\text{H}_3\text{Cl}_3$	CO_2
$\text{C}_2\text{H}_6\text{ClN}$	$\text{C}_2\text{H}_2\text{O}_4$
$\text{C}_2\text{H}_5\text{Cl}_2\text{N}$	$\text{C}_2\text{H}_6\text{O}$
PCl_3	$\text{C}_5\text{H}_{12}\text{O}$
NH_4Cl	$\text{C}_4\text{H}_6\text{O}_4$
CrO_2Cl_2	$\text{C}_3\text{H}_8\text{O}_3$
SO_2Cl_2	$\text{C}_2\text{H}_3\text{OCl}$
SO_4H_2	$\text{C}_2\text{H}_4\text{OCl}_2$
PO_4HNa_2	
PbO_2H_2	
PbO	
PbO_2	

There are, however, some cases which at first sight do not agree with this general conclusion. Thus, on comparing potassic chloride with potassic oxide, it might be said that the equivalent weight of potassium in the former is combined with an equivalent weight of chlorine, and in the latter with an equivalent weight of oxygen; thus KCl , KO_2 . But the answer is that this comparison is made in defiance of the known molecular formula of potash (K_2O), established by reactions and analogies which leave no doubt of its correctness. Whenever oxygen replaces chlorine in such a chloride, it binds together two basic equivalents, one from one molecule of the chloride one from another; and in like manner when chlorine replaces oxygen in any molecule, such as water H_2O or potassic hydrate, it loosens into two molecules what the oxygen held bound up in one. Thus, by passing oxygen and hydric chloride through a red-hot tube, we have a replacement of chlorine by oxygen, taking place, as far as it goes, according to the molecular equation $\text{O}_2 + 4\text{HCl} = 2\text{H}_2\text{O} + 2\text{Cl}_2$, half as many molecules of water being formed as molecules of hydric chloride are decomposed; and on the other hand if we send chlorine and steam through a hot tube, we break up a part of the steam, forming two molecules of chloride from every one of oxide.

When we apply the word atom to two equivalent weights of oxygen, and say that an atom of oxygen has a replacing value equal to that of two atoms of chlorine or of hydrogen, we give to a couple of equivalent weights of oxygen the name atom, as a record of the fact that we have never known them to divide, and that we must in all our considerations respecting oxygen bear in mind this peculiarity of it. In carbonic oxide it may be argued that an atom of oxygen takes the place of four equivalents of hydrogen of marsh-gas, and that it has there the equivalent weight 4, instead of its usual equivalent weight 8. But on the other hand the gas may be represented as containing carbon with an equivalent weight of double its usual one, viz., 6 instead of 3. In any case, the gas affords an instance of a change of atomic value, and if we describe the value of the atom of oxygen in disregard of this case, it is because we have to record its commonest value.

What has been here said of oxygen applies to sulphur equally. No molecule has ever been found containing an uneven number of equivalent weights of sulphur, and the atom of sulphur has

certainly the value of two chlorine or hydrogen. There are, however, strong reasons for believing that in some of its compounds its atom has a replacing value of four or even six. Selenium and tellurium are so closely allied to oxygen and sulphur in their reactions that their atoms are always classed together. In like manner bromine and iodine go with chlorine, and lithium, sodium, &c., go with hydrogen and potassium. Silver also has an atom of uneven value.

Nitrogen is found upon similar evidence to divide in no smaller proportion than that of three times $4\frac{2}{3}$, or 14 parts by weight, for whenever it has an equivalent weight of $2\frac{1}{3}$, as in NH_4Cl , its atom has five values.

It seems to me of paramount importance to the due understanding of the functions of this element, to state in the most direct and matter of fact way possible, the actual proportion in which its atom replaces hydrogen. If the replacing value of an atom be measured by the number of hydrogen atoms needed to replace it, then nitrogen has in ammonia the atomic value three, for three atoms of hydrogen are needed in order to replace one of nitrogen in NH_3 , forming three molecules of hydrogen H_3H_3 ; and in sal ammoniac it has just as distinctly the atomic value five, for five atoms of hydrogen are needed in order to take the place of one of nitrogen, forming one molecule of hydric chloride

and four molecules of hydrogen: ClNH_4 becomes $\text{ClH} + \overline{\text{H}_4\text{H}_4}$. Sal-ammoniac is as well known a molecule as ammonia itself; each of them undergoes decomposition at high temperatures, the complex molecule not requiring so high a temperature for its decomposition as the simpler one. Those chemists who represent sal-ammoniac as containing one atom of nitrogen of the same value as in ammonia, seem to me to incur the disadvantage of stating rather what, according to their own theoretical notions *ought* to be, than what actually *is*, and thereby to lose sight of one of the most important of all properties of atoms, viz., the property of changing value under particular chemical and physical conditions which it is our business to study and describe.

I shall return to this important point somewhat later, and endeavour to trace an outline of the conditions of these changes.

Together with nitrogen are always classed the elements phos-

phorus, arsenic, antimony, and bismuth. Their atoms have frequently the value of three, but frequently also that of five. Boron has in its chloride and fluoride the value three, but in its double fluoride the value five— BCl_3 , BF_3 , KBF_4 . Gold is not proved to have any smaller atomic value than three, for we have no evidence of the molecular weight of the compound AuCl . Compounds corresponding to AuCl_3 and NaAuCl_4 , are common and tolerably well known.

Carbon is at present perhaps that element of which the compounds are best investigated. A comparison of the composition of an immense number of carbon-compounds has not led to the discovery of a single molecule containing a number of its equivalent weights, other than such as can be divided by four. Its atom is accordingly considered to weigh 12, and to have the value 4. In carbonic oxide, the atom of carbon has a somewhat uncertain value, according as we consider oxygen to vary in value or not. Silicium, titanium, and tin are in many respects so closely allied to carbon that it is to be expected that their atomic weight must be such as to give the atoms the value 4 in their ordinary compounds. The atom tin in stannous chloride appears at first sight to be worth 2, but the molecular formula of the compound is not known, and may possibly be Sn_2Cl_4 like olefiant gas. Silicium in its double fluoride, SiF_6K_2 , is evidently worth 8, and titanium and tin have also doubtless a higher value than 4 in their double salts.

Platinum seems to vary from four values to eight, as in the compounds PtCl_4 and PtCl_6K_2 . Its lower chloride PtCl_2 ought probably to have a higher molecular formula.

Not only does the empirical comparison of the number of equivalent weights of each element contained in well-known molecules lead to a discovery of the relative weights of atoms, but there are other chemical evidences which concur with these. Thus the univalent alkali-metals have long been known to be unable to form basic salts, whereas many multivalent metals form such salts with peculiar facility; witness antimony and bismuth, mercury and lead, in the compounds SbOCl , $\text{Bi}_2\text{O}_2\text{SO}_4$, $\text{Pb}(\text{HO})(\text{NO}_3)$. In such compounds as these, the metal performs the function of binding together several radicals or simple atoms, just as in water or potassic hydrate the oxygen binds the two atoms together; and when such a metal is removed, and an equivalent quantity of a single-

value metal supplied in its place, the atoms which had been bound together pass off, each in combination with its own atom of metal. Thus, in the reaction $\text{Pb}^{\text{HO}}_{\text{NO}_3} + \text{Ag}_2\text{SO}_4 = \text{PbSO}_4 + \text{AgOH} + \text{AgNO}_3$ we have a severance of AgOH from AgNO, which would not take place if silver were of double its atomic weight, and, like lead, of the atomic value 2.

Double amides, such as $\text{Hg}^{\text{Cl}}_{\text{NH}_2}$, and double salts, such as $\text{Ba}^{\text{NO}_2}_{\text{C}_2\text{H}_3\text{O}_2}$, $\text{Cu}^{\text{AsO}_2}_{\text{C}_2\text{H}_3\text{O}_2}$ are also evidences of the biacid character of the base, just as $\text{KNaC}_4\text{H}_4\text{O}_6$ is an evidence of the bibasic character of the acid.

Again, compounds of metals with organic radicals have furnished admirable evidences of the atomic weights of various metals whose equivalent weights are known. Thus the compounds $\text{Zn}(\text{C}_2\text{H}_5)_2$, $\text{Zn}^{\text{C}_2\text{H}_5}_1$, $\text{Hg}(\text{C}_2\text{H}_4)_2$, $\text{Hg}^{\text{C}_2\text{H}_5}_1$, $\text{Sn}(\text{C}_2\text{H}_5)_4$, $\text{Sn}^{\text{C}_2\text{H}_5}_3$, $\text{Sn}^{\text{C}_2\text{H}_5}_2$, $\text{Pb}(\text{C}_2\text{H}_5)_4$, $\text{Pb}^{\text{C}_2\text{H}_5}_3$, &c., have been among the best chemical evidences of the atomic values of the respective metals.

Similar proofs of the value of the atom of silicium have been given by the formation of molecules containing atoms of ethyl and chlorine together numbering *four*, just as in the molecule of marsh-gas the hydrogen can be replaced by chlorine in four distinct proportions.

Atomic Heat.

Perhaps the most direct confirmation of the atomic weights established upon evidence of the various kinds which we have been considering is afforded by the capacity for heat of elementary bodies. A comparison of the relative capacity for heat of solid elements showed that all atoms have nearly the same capacity for heat. Thus 23 grammes of sodium absorb, when heated from 0°C. to 1°C. , almost exactly the same quantity of heat as 39 grammes of potassium when heated from 0°C. to 1°C. ; and 210 grammes of bismuth absorb that same quantity when heated from 0°C. to 1°C. Silicium, carbon, and boron form exceptions to this law, but in all other cases the approximation

to equality between the numbers found for the several solid elements is admitted to be as close as can be expected from determinations involving so many difficulties, and including so many sources of error.

Like every other confirmation of the atomic theory, the law of atomic heat has contributed to the development and systematisation of that theory. It is well known that a considerable number of metals, such as lead, mercury, iron, tin, barium, &c., appeared, according to the atomic weights originally assigned to them, to have about half the atomic heat of the metals before mentioned, and that this circumstance was urged by an illustrious Italian chemist as an argument for doubling their atomic weights, so as to bring them within the law. It is also too well known to need illustration to you, that the chemical properties of those metals amply confirm the truth of Cannizzaro's proposition, that their atomic weights are twice as great as was formerly supposed. Indeed so much chemical evidence has now been accumulated, that we should certainly retain the higher atomic weights for lead, tin, iron, barium, &c., even if we knew nothing of atomic heat.

Atomic values are not so variable as equivalent weights. A most important light has been thrown on the phenomena of equivalence by our knowledge of atomic values and the general principle of their changes. The foundation of this consideration was laid by those chemists who proved that the molecule of chlorine consists of two atoms of chlorine combined with one another, and that the molecule of oxygen consists of two atoms of oxygen combined with one another.

It is well known that free carbon at high temperatures unites with hydrogen, forming acetylene, which has the molecular formula C^2H_2 . I will write the number belonging to each atomic symbol above, as an exponent, when I wish to represent the atoms so numbered as combined with one another, O^2 , &c., meaning a compound of an atom of oxygen with an atom of oxygen; C^2 a compound of an atom of carbon with another atom of carbon. On the other hand, I will write the number belonging to any atomic symbol below, when I wish to represent the atoms as not combined with one another. Thus H_2 means two atoms of hydrogen, and OH_2 means a compound of one atom of oxygen with two atoms of hydrogen, each of

which atoms of hydrogen is merely united with the atom of oxygen. It is merely an abbreviated form of writing HOH or

$$\begin{array}{c} \text{HO} & \text{H} \\ & | \\ \text{H} & \text{or O \&c.} \end{array}$$

By adding two atoms of hydrogen to acetylene

we get olefiant gas, C^2H_4 , and this again, in its turn, can be transformed into methyl C^2H_6 . These bodies, C^2H_2 , C^2H_4 , C^2H_6 , are well known to have molecular weights corresponding to two atoms of carbon in each, and the hydrogen is held in each molecule by being combined with the carbon. With more hydrogen the double atom of carbon cannot combine, for the next hydrocarbon to methyl is marsh-gas CH_4 containing a single atom of carbon.

Again, if we remove hydrogen from marsh-gas in the smallest possible proportion, we find that the atom of carbon in one molecule combines with one atom of carbon in another molecule, while they are losing their hydrogen. Methylic iodide reacts on zinc-iodomethide by a normal interchange of iodine for methyl $\text{H}_3\text{CI} + \text{IZnCH}_3 = \text{H}_3\text{CCH}_3 + \text{ZnI}_2$. It is admitted that the explanation of the molecular weight of methyl lies in the fact that it contains two atoms of carbon combined with one another to the extent of one-quarter of their value, and that this combination of carbon with carbon is the essential condition for the formation of such a complex molecule. But, if this be true, the other terms of the series are explained by a mere extension of the same principle. Ethylene contains two atoms of carbon H_2CCH_2 , each combined with two atoms of hydrogen, and each one combined with the other to the extent of two of its values. Acetylene, HCCII , is in like manner a compound of two atoms of carbon, each one combined with the other to the extent of three values.

It was known that an atom of carbon may combine partly with hydrogen, partly with some other element or elements, and it was also known that like atoms combine with one another; so that it was quite consistent with known facts to suppose that an atom of carbon may combine partly with another atom of carbon, partly with some other element. The simplification introduced into the chemistry of the compounds of carbon by this theory is, however, truly admirable, and, by itself, entitles the distinguished author of the idea to the high rank among theorists which he holds.

Carbon in all its compounds may have the same atomic value consistently with our present knowledge of those compounds. In carbonic oxide alone we are compelled to represent it as having only the value two, unless we attribute to oxygen the value four.

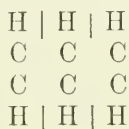
Among the instances of increase of equivalent weight in elements, there are a great number in which the element exhibiting that increase, by giving up some of the unlike with which it was united, unites with the like while doing so.

Thus, SCl_2 , by the mere action of heat, decomposes with evolution of chlorine, and by an atom of sulphur combining with another atom of sulphur, $2\text{SCl}_2 = \text{S}_2\text{Cl}_2 + \text{Cl}_2$. Water and hydric peroxide are doubtless related to one another, in the same manner, each of the two atoms of oxygen in the molecule of the peroxide being half combined with oxygen, half with hydrogen. Mercuric chloride loses half its chlorine, forming calomel, while the mercury unites to the extent of half its value with mercury, and cupric chloride is reduced to cuprous chloride by a similar process. On the other hand, phosphoric chloride loses chlorine, and forms phosphorous chloride, without any combination of phosphorus with phosphorus taking place. The equation $\text{PCl}_5 = \text{PCl}_3 + \text{Cl}_2$ represents the process; and until it can be shown that the molecule of phosphorous chloride is a multiple of PCl_3 , the reaction must be accepted as direct evidence of a change in the atomic value of phosphorus from 5 to 3. In like manner, if ammonia be admitted to have the molecular formula NH_3 , the decomposition of sal-ammoniac by heat, according to the equation $\text{ClNH}_4 = \text{NH}_3 + \text{HCl}$, must be admitted as evidence of a change of atomic value in nitrogen from 5 to 3. When auric chloride is decomposed, with evolution of chlorine and formation of aurous chloride, the interpretation of the reaction requires evidence which we do not possess respecting the molecular weight of the lower chloride. If aurous chloride has the molecular formula AuCl , its formation is accompanied by a change of atomic value in the gold; but if its molecule contains more than one atom of gold, the metal may exist in both compounds with the same atomic value.

Among complex organic molecules there is, of course, considerable room for variety in the arrangement of atoms, which we may consider consistently with the empirical equivalent weight of the carbon.

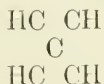
The hydrocarbon benzole is of so much interest from its derivatives, that it has attracted a good deal of attention, and to explain its molecular constitution, the six atoms of carbon have been represented as arranged in a ring, each atom being combined with the atom of carbon at one side of it to the extent of two values, and with the atom of carbon on the other side of it to the extent of one value.

Another arrangement, which was mentioned a good many years ago at this Society, is to consider each atom of carbon combined with three others, and with one atom of hydrogen. Such an arrangement is easily represented in space. Let the accompanying formula represent as unfolded in one plane, the group which would be formed by the carbon atom at one end of each line moving back through the paper until equidistant from the two others in the line.



I put bars between symbols of elements, which, for convenience, are juxtaposed, but which I do not wish to represent as combined with one another.

Naphthalin may, in like manner, be represented by the formula C^5H_4 , as containing four atoms of carbon, each united with two of the others and with one atom of hydrogen, while the fifth atom of carbon is combined with each of the first four.



With respect to the conditions under which changes of atomic value take place, some valuable information may be gained by comparing molecules known to exist in different states. Let any chemist write for himself a list of molecules known to exist in the liquid state alone, and not volatile without decomposition. Let him compare with that, a list of molecules known to evaporate unchanged; and thirdly, let him look at the molecular formulæ of the hitherto uncondensed gases. He will notice that in passing from the non-volatile to the uncondensed, he goes from complex molecules to simpler and

simpler ones. Let him compare the formulæ of products formed by destructive distillation with those of the materials from which they are formed. The examples may be taken from mineral and from organic chemistry. He will find some cases of the formation of a more complex molecule by distillation; but for one such he will find an enormous number of cases of the breaking up of complex molecules into more and more simple ones. Take, for instance, the series CO_3H_2 , SO_3H_2 , NH_5O , SbCl_5 , PCl_5 , SO_4H_2 , PO_4H_3 , $\text{C}_2\text{O}_4\text{H}_2$, NH_3 , CH_4 , H_2O , CO_2 , beginning with compounds so exceedingly unstable, that, working at ordinary temperatures, we hardly know them; and finishing by compounds of great stability, which are only broken up into simpler molecules at the most intensely high temperatures. The fact stares us in the face, that simple molecules correspond to high temperatures, complex molecules correspond to low temperatures. Several of these changes of composition are certainly accompanied by changes of atomic value. Whenever there is a change of atomic value effected by change of temperature, the lower atomic value corresponds to the higher temperature. These phenomena have attracted some attention of late, in consequence of Deville's researches on dissociation. I will give an example of the application of this principle to the study of reactions in illustration of the importance of seeing and recording differences of atomic value in elements.

I will again use the notation which I referred to above. The following formulæ give samples of nitrogen-compounds in which nitrogen has the atomic value 5: ClNH_4 , HONH_4 , $\text{HON}(\text{C}^2\text{H}_5)_4$, $(\text{H}_4\text{NO})_2\text{CO}$, $(\text{H}_4\text{NO})_2\text{C}^2\text{O}_2$, H_4NOCCH_3 . The action of heat

upon them gives rise to NH_3 in two cases, $\text{N}(\text{C}^2\text{H}_5)_3$, $(\text{H}_2\text{N})_2\text{CO}$, $(\text{H}_2\text{N})_2\text{C}^2\text{O}_2$, H_2NCCH_3 . In each case the nitrogen-atom is

reduced to the value of 3. In fact it will be seen that in ammonium-salts nitrogen is worth 5, in amides only worth 3. Ammonia is an amide in this sense.

Among chemical evidences of atoms, the discovery of the distinction between direct and indirect combination is worth consideration, more especially as it is independent of the quantitative comparisons which have hitherto guided us. Many elements which have never been obtained directly combined, are bound together by a third; thus we have no direct com-

pound of hydrogen and potassium, but in potassic hydrate an atom of hydrogen is united with oxygen, and an atom of potassium is united with this same oxygen HOK . Hydrogen in this hydrate is indirectly united with potassium, an atom of oxygen being the connecting link between them.

Some elements can be either directly or indirectly united with one another, and exhibit different properties in each condition. In organic compounds we know an immense number in which hydrogen is directly united with carbon. Thus, methylic oxide H_3COCH_3 has all its six atoms of hydrogen united with carbon directly, whilst vinic alcohol H_3CCOH has five of its

H_2

atoms of hydrogen united with carbon directly, and one atom indirectly, through oxygen.

In consequence of this difference, we find that the hydrogen, which is indirectly united with carbon through the intervention of oxygen, separates from it as soon as by any process the oxygen is replaced by chlorine or bromine; whereas the hydrogen which is directly united with carbon undergoes no change by such replacement. H_3COCH_3 by the action of PCl_5 becomes $\text{H}_3\text{CCl} + \text{ClCH}_3$, whereas H_3CCOH becomes H_3CCCl

H_2 H_2

+ ClH . When the hydrocarbons are liberated from these compounds, it is well known that a direct combination of carbon in one atom with carbon in another takes place, as in the formation of C^2H_6 from a methyl-compound, or $\text{H}_3\text{CCCCCH}_3$ from an ethyl-compound.

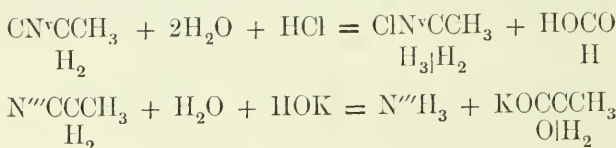
In like manner to oxygen, an atom of zinc holds two atoms of ethyl in combination in the molecule $\text{H}_3\text{CCZnCCH}_3$, and by the action of water, the atom of zinc is replaced by two atoms of hydrogen, each atom of ethyl getting an atom of hydrogen in exchange for the half-atom of zinc which it held at first.

These and many similar reactions are now so familiar to chemists that I only allude to them to recall their bearing on the order of combination of atoms.

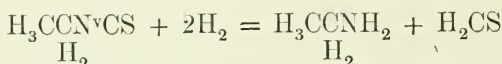
Not only are they known and admitted to be due to differences of arrangement, such as I have alluded to, but the idea which they have established is found a sure and faithful guide in the investigation of the intricate varieties presented by isomeric organic bodies in their varied reactions.

Thus it is well known from Hofmann's admirable researches on the isomeric cyanides and sulphocyanates, that, by the action of ethylia on chloroform, an ethylic cyanide is formed, isomeric with the compound formerly known. It breaks up by the action of hydric chloride in presence of water, into hydric formate, and the compound of ethylia and hydric chloride, instead of breaking up, as the other cyanide does, under the influence of alkalis, into ammonia and a propionate.

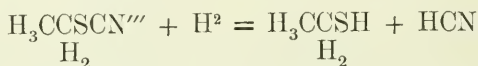
The following equations represent the two reactions :—



And in like manner his new sulphocyanates break up under the influence of nascent hydrogen, according to the equation—



whilst their isomerics on the SH_2 type break up thus :—



In the new cyanides, the carbon of the cyanogen is indirectly united with the carbon of the ethyl through an atom of nitrogen of the value 5; whereas, in the old cyanide of ethyl, the carbon of the cyanogen is directly combined with the carbon of the ethyl, and in the sulphocyanate carbon is indirectly combined with carbon through the intervention of sulphur.

What concerns us in these reactions is to see the evidence which they afford, that the binding element is an atom. The very fact itself amounts to that. In potassic hydrate, oxygen is combined with hydrogen; it is also combined with potassium, but the hydrogen cannot pass off, even at a red heat, in combination with its half of the oxygen. The two halves are inseparable, and when I say that in the molecule of potassic hydrate there is a single atom of oxygen, I merely state that fact.

I would gladly proceed now to other and certainly not less interesting considerations based upon the atomic theory, which

have received verification from experiment, considerations for which I think it would be at least rather difficult to find any equivalent if matter were not composed of atoms; but I must content myself with indicating them at present, and reserving for a future occasion the task of giving more development to them. I allude to atomic motion—the dynamics of chemistry. It has been shown that heterogeneous molecules, when mixed with one another in the fluid state, interchange their analogous constituents, and that the products thus formed, if they remain mixed in the fluid state, also exchange their analogous constituents, reproducing the original materials. In a solution of two salts there are formed two new salts by the exchange of bases; and it depends on the relative velocities with which the decomposing change and the reproducing change go on in the liquid, what proportion the quantity of the original materials bears in the final mixture to that of the new products.

In using the atomic language and atomic ideas, it seems to me of great importance that we should limit our words as much as possible to statements of fact, and put aside into the realm of imagination all that is not in evidence. Thus the question whether our elementary atoms are in their nature indivisible, or whether they are built up of smaller particles, is one upon which I, as a chemist, have no hold whatever, and I may say that in chemistry the question is not raised by any evidence whatever.

They may be vortices, such as Thomson has spoken of; they may be little hard indivisible particles of regular or irregular form. I know nothing about it; and I am sure that we can best extend and consolidate our knowledge of atoms by examining their reactions, and studying the physical properties of their various products, looking back frequently at the facts acquired, arranging them according to their analogies, and striving to express in language as concise as possible the general relations which are observed among them.

In conclusion I must say that the vast body of evidence of the most various kinds, and from the most various sources, all pointing to the one central idea of atoms, does seem to me a truly admirable result of human industry and thought. Our atomic theory is the consistent general expression of all the best known and best arranged facts of the science, and certainly it is the very life of chemistry.

XXXII.—*On Ethylbenzoic Acid.*

By A. KEKULÉ and T. E. THORPE.

ETHYLBENZOIC acid, $C_6H_4 \begin{Bmatrix} CO_2H \\ C_2H_5 \end{Bmatrix}$, was first synthetically obtained by one of us about four years ago, from ethylbenzol, according to the method by which he then prepared benzoic, toluylie, and xylylic acids;* this acid, however, was not at the time more accurately investigated. Subsequently Fittig and König† have also obtained ethylbenzoic acid by the oxidation of diethylbenzol by means of nitric acid. The two acids must necessarily be identical, since the monobromethylbenzol served as the starting point in each case. Indeed Fittig and König were disposed to regard the two acids as identical, although it appears that they entertained some degree of doubt concerning the success of the synthetical experiments.

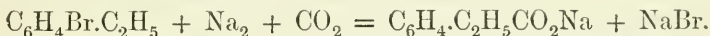
We considered it necessary, however, to submit this question of identity to experimental proof, and accordingly we have more closely investigated a quantity of the acid obtained from the former preparation, and at the same time we have prepared a fresh amount, according to the method above referred to, that is, by allowing carbonic acid and sodium to act simultaneously upon monobromethylbenzol.

A quantity (about 20 grms.) of the bromide, $C_6H_4BrC_2H_5$, is placed in a comparatively large flask, and diluted with six or seven times its volume of perfectly anhydrous ether, so that the mixture covers the bottom of the flask to a depth of about half an inch; the theoretical quantity of sodium cut into slices as thin as possible is next added, and a slow continuous current of carbonic acid is then sent through the liquid; the apparatus is attached to a condenser in such a manner that the condensed portion may return to the flask, and if necessary the action is regulated by immersing the flask from time to time in cold water. In about 24 hours the process is completely finished. The dark green slimy mass is next repeatedly treated with ether, the excess of sodium carefully removed, the salt dis-

* Kekulé, *Ann. Chem. u. Pharm.*, 137, 178.† Fittig u. König, *Ann. Chem. u. Pharm.*, 143, 288.

solved in a small quantity of water, and the solution filtered. The acid is then precipitated by the addition of a slight excess of hydrochloric acid, separated by filtration, and washed slightly with a small quantity of cold water. In order to purify it, the mass is next dissolved in warm baryta-water, the excess of baryta removed by a current of carbonic acid gas, the solution filtered, and the acid again precipitated from the warm solution by hydrochloric acid. The acid is once more dissolved in baryta-water, and the above process repeated; on the third precipitation by hydrochloric acid, the substance is obtained perfectly pure.

The reaction which occurs in the synthesis of ethylbenzoic acid may be represented as follows:—



Practically, however, the reaction appears to be far more complicated than is represented by the above equation. Although in all cases the same amounts of the bromide of sodium and of ether were employed, still the quantity of acid obtained in successive operations varied very considerably. We have not studied the conditions under which the acid is formed, with the accuracy necessary to enable us to state the causes of these differences; it would appear, however, that the presence of a small quantity of moisture favours in some unknown manner the production of the sodium salt.

The acid thus prepared is identical in every particular with the ethylbenzoic acid described by Fittig and König. It crystallises from boiling water in small leaflets, which possess a considerable degree of resemblance to benzoic acid. Its solubility in cold water is considerably less, however, than that of the latter acid. The pure acid melts at 110° — 111° (Fittig and König, 110° — 111°), and on cooling solidifies to a confused crystalline mass. It begins to sublime a few degrees below its melting point, and when heated with a quantity of water insufficient for its complete solution, melts to a heavy, colourless oil. The acid is easily soluble in alcohol and ether. The acid prepared by repeated crystallisation from alcohol invariably melted 3° — 4° lower than that purified by recrystallisation from water.

The barium salt $\text{Ba}(\text{C}_9\text{H}_9\text{O}_2)_2 + 2\text{H}_2\text{O}$, prepared by neutralizing the acid with barium carbonate, crystallises with difficulty

in plates. It dissolves in about 45 parts of cold water, but far more easily in hot water. It loses its water of crystallisation when placed over sulphuric acid.

0.5637 grm. of the air-dried salt, lost on drying at 120° , 0.0430 grm. water, and gave 0.2633 grm. barium sulphate.

	Calculated.		Found.
$2(\text{C}_9\text{H}_9\text{O}_2)$	298	63.28	—
Ba.....	137	29.10	29.4
$2\text{H}_2\text{O}$	36	7.62	7.63

The copper salt $\text{Cu}(\text{C}_9\text{H}_9\text{O}_2)_2$ is a bluish green amorphous powder, nearly insoluble in water, obtained by adding copper sulphate to a dilute solution of sodium ethylbenzoate.

0.2218 grm. of the salt, dried at 130° , gave—

0.4827 grm. carbonic acid,

0.1004 grm. water, and

0.0489 grm. copper oxide.

	Calculated.		Found.
C_{18}	216	59.75	59.34
H_{18}	18	5.00	5.02
Cu.....	63.5	17.57	17.61
O_4	64	17.68	—

The above experiments conclusively prove that the acid obtained synthetically from ethylbenzol is identical with that obtained by Fittig and König by the oxidation of diethylbenzol.

XXXIII.—On Hydrofluoric Acid.

By G. GORE, F.R.S.

(From the Philosophical Transactions, 1869, p. 173.)

A. Anhydrous Hydrofluoric Acid.

THE method I have adopted to obtain this compound is the same as that employed by Fremy*, viz, to heat to redness dry double fluoride of hydrogen and potassium in a suitable platinum apparatus.

* Ann. de Chimie (3), vol. xlvii, p. 5; Comptes Rendus, No. 9, Feb. 27th, 1854.

As the results I have obtained differ somewhat from those described by Fremy, and as the anhydrous acid has been considered to be a *gas* by him and by several other able investigators*, it will be necessary for me to state with a sufficient degree of minuteness the conditions of my experiments.

Pure aqueous hydrofluoric acid, prepared by the method described in this paper (page 400), and free from sulphuric, sulphurous, hydrosulphuric, hydrochloric, and hydrofluosilicic acid, also from sulphur, arsenic (except minute traces), and all fixed substances, was added to carbonate of potassium (free from chlorides, sulphates, and silica) in a large platinum dish, until the liquid on evaporation evolved a distinct acid odour, and the vapour reddened litmus-paper. The clear solution was evaporated to perfect dryness, and the residue gently heated until it fused to a clear thin liquid, free from films upon its surface; it evolved a trace of acid vapour during the process, and did not corrode the platinum vessel. The salt when cooled formed a rather hard, white, non-deliquescent mass; but if the acid was in much excess, the fused salt had tough films upon its surface, and formed on cooling a less hard, less white and more transparent mass.

To obtain the acid from this salt, about 2800 grains weight of fragments of the substance was put into a platinum retort of the annexed form (fig. 1), about 6 inches (= 15·3 centimetres) deep and $1\frac{1}{2}$ inch (= 3·8 centimetres) diameter, and gently heated to complete fusion to expel any traces of water. The vessel was then fitted airtight (by means of melted sulphur mixed with lampblack) to a closely fitting platinum tube, about 36 inches (= 91·5 centimetres) long, of a Liebig's condenser, A (fig. 3), the condenser being supplied with a freezing-mixture, composed of 1 part of pounded ice and $1\frac{1}{2}$ part of

Fig. 1.

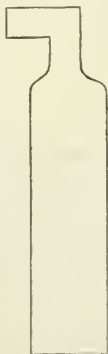
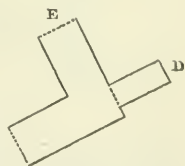


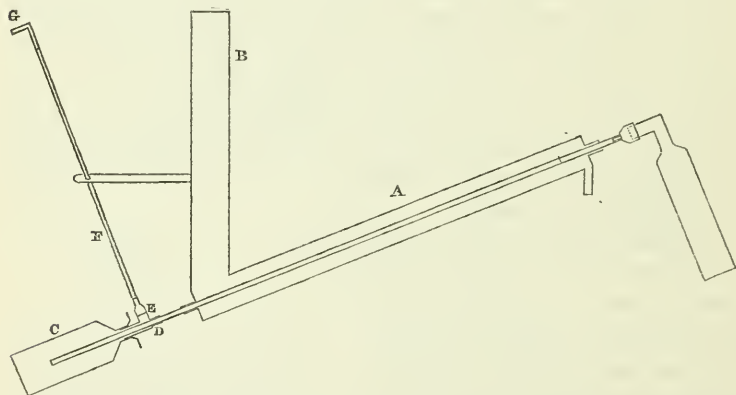
Fig. 2.



* Vide Fremy, Comptes Rendus, No. 9, Feb. 27th, 1854; Louyet, Comptes Rendus, vol. xxii, p. 960; also Miller, Elements of Chemistry, part 2, 4th edition p. 161.

crystallised chloride of calcium, through the open tube B. A platinum bottle, C, immersed in a similar freezing-mixture, was employed to receive the distillate. The bottle was provided with a three-necked angle-tube of platinum (see fig. 2), through the narrow opening, D, of which the condensing-tube passed into the bottle, and the angle-tube had a long exit-tube of platinum, F, fixed upon its larger opening, E. The exit-tube had upon its upper end a short angle-tube of platinum, G, turned downwards to prevent attracted moisture running down into the bottle (see fig. 3)*. The tubes all fitted tightly, and the *cold* junctions were made gas-tight by means of a mixture of melted paraffin and lampblack†.

Fig. 3.



Heat was now gradually applied and the acid rapidly distilled until (in about twenty minutes) the bottom of the retort became red-hot, indicating a completion of the process. The materials bumped considerably towards the end of the process (this may be diminished by applying the heat to the *side* of the retort), and a small quantity of the salt was carried mechanically over. The freezing-mixture is indispensable, and careful

* All the platinum apparatus used in this investigation was constructed for me with great care by Messrs. Matthey and Co., and without such apparatus the experiments could not possibly have been made.

† Paraffin answers admirably for resisting hydrofluoric acid where heat is not applied; it may easily be formed into stoppers, cups, plates, rods, and almost any desired shape; it is, however, liable to become full of cracks when suddenly immersed in a freezing-mixture. Temporary stoppers were conveniently made by melting paraffin in a test-tube, and then breaking the tube.

management of the heat is required. Care must be taken to have all parts of the apparatus quite free from moisture, and also from traces of fluoride of potassium, which is highly deliquescent, and is acted upon with dangerous violence by the acid. The acid was redistilled without exposing it to the air, the retort being immersed in a bath of slightly warm water, kept at a temperature not exceeding 100°F. ; under these circumstances any trace of water contained by the acid was retained in the retort by the small quantity of saline matter. 2800 grains of the acid usually carried over mechanically about 5 or 10 grains of saline matter in the first distillation.

The acid thus obtained is a highly dangerous substance, and requires the most extreme care in its manipulation*: it left no fixed residue on evaporation: it was a perfectly colourless and transparent liquid at 60°F. , very thin and mobile, extremely volatile, densely fuming in the air at ordinary temperatures, and attracted water greedily from the atmosphere. It was perfectly retained in platinum bottles, the bottles having a flanged mouth, a platinum plate coated on its lower side with the paraffin mixture (see page 370) being tightly secured to the flanged mouth by eight clamp-screws (see fig. 4). The acid must be kept in a cool place, not above a temperature of 60°F. , otherwise it is very likely to burst the bottle; and a freezing-mixture should always be at hand whilst experimenting with it.

Fig. 4.



According to Louyet† anhydrous hydrofluoric acid, obtained by distilling oil of vitriol and fluor-spar, and redistilling the condensed product with anhydrous phosphoric acid, is a *gaseous* substance, and does not liquefy at -12°C. ($= +10^{\circ}\cdot4\text{F.}$) under ordinary atmospheric pressure; it fumes very strongly in the air, is rapidly condensed by water, has scarcely any action upon glass, and might probably be collected in glass vessels

* The highly dangerous nature of the anhydrous acid has received further confirmation in the recent sudden death of Professor Nicklès, of Nancy, which, according to the *Moniteur Belge* of April 14th, 1869, was occasioned by accidentally inhaling the vapour of the concentrated acid whilst engaged in making experiments to isolate fluorine.

† *Comptes Rendus*, vol. xxii, p. 960; also *Gmelin's Handbook of Chemistry* vol. ii, p. 361.

over mercury. According to Fremy* (who states that he assisted at the performance of M. Louyet's experiments, and did not consider the results satisfactory), the dehydration effected by means of anhydrous phosphoric acid is not complete. He states that anhydrous hydrofluoric acid obtained by the distillation of dry double fluoride of hydrogen and potassium is *gaseous* at the ordinary temperature, but may be condensed at -20° C. by a mixture of ice and salt; it is then a very fluid liquid, volatilizing when removed from the cooling mixture, acting very powerfully upon water, diffusing white fumes in the air with an intensity like that of fluoride of boron, and, contrary to M. Louyet's assertion, attacks glass rapidly.†

To ascertain, therefore, whether the liquid I had thus obtained was really anhydrous or not, I made the following analytical experiments:—1st. I took 100 grains of the recently and well dried double fluoride (which soon attracts a little moisture from the air), and heated it gently, with constant motion, in a platinum dish until it was all fused; it evolved an acid odour, and lost 0.8 grain in weight. I now again slowly fused it, gradually increasing the heat until at an incipient red heat it was quite solid and evolved no more acid odour, then cooled it under a cover and weighed quickly; its loss was now increased to 25.57 grains, the calculated theoretic loss of anhydrous hydrofluoric acid being 25.59 grains, assuming the salt to be KF, HF.

$$K = 39.1$$

$$F = 19.0$$

$$HF = 20.0$$

$$KF, HF = 78.1$$

Berzelius found 25.1 per cent. of volatile matter in this salt, and also by heating the salt with six times its weight of protoxide of lead obtained 11.6 per cent. of water = 1.288 per cent. of hydrogen in it; theory requires 1.280 per cent.‡ In a second trial 800 grains of the salt, which had been previously fused,

* Comptes Rendus, No. 9, Feb. 27th, 1854; also The Chemist, June, 1854.

† Fremy also obtained the anhydrous acid by heating fluoride of lead (contained in a charcoal boat within a platinum tube) in a current of dry hydrogen, and Deville obtained the dry acid by passing hydrochloric acid gas over highly heated fluor-spar (Comptes Rendus; also Chemist, new series, vol. iv, p. 330, and vol. ix p. 556).

‡ Gmelin's Handbook of Chemistry, vol. iii, p. 65.

was gradually heated to redness; it lost 204·6 grains (= 25·575 per cent.), the theoretic quantity of HF being 204·78 grains. In a third experiment 2063·6 grains of the salt, which had not been sufficiently heated, lost 547 grains (including a little saline matter) in the process of distillation (it should have lost only 528 grains); for the analysis of the acid obtained from it see page 376.

2nd. I took another 100 grains of the same salt, dissolved it in water in a capacious platinum dish, added $1\frac{1}{2}$ ounce of pure and strong hydrochloric acid, and evaporated nearly to dryness, then added more of the acid and slowly heated to perfect dryness, and finally to low redness; the weight of the residue was 95·45 grains, theory requiring 95·47 grains of chloride of potassium.

3rd. I now made several attempts to determine the amount of fluorine in the salt by means of silica. I took 78·2 grains of the perfectly dry salt, reduced it to fine powder, added 50 grains of pure precipitated silica (which was previously found to lose no weight by being boiled in strong sulphuric acid), and mixed them together in a platinum bottle; then added in small portions at a time a quarter of an ounce by measure of strong sulphuric acid, and after awhile applied heat gradually until the sulphuric acid was considerably expelled. The residue was then thoroughly washed in a filter, dried, heated to redness, and weighed; it amounted to 19·3 grains = 30·7 grains dissolved = 38·56 grains of fluorine, theory requiring 38·05 grains. In a second similar experiment, 29·8 grains of silica was dissolved; in a third, with 40·7 grains of silica, 29·6 grains was dissolved; in a fourth experiment, with 100 grains of silica and half an ounce of the acid, 30·1 grains was dissolved; and in a fifth experiment, with 50 grains of silica, and a quarter of an ounce of water added before addition of the acid, 31·3 grains was dissolved: this addition of water appeared to facilitate the action by rendering the mixture more fluid, and also by retaining the liberated hydrofluoric-acid gas in solution until it had time to act upon the silica. The average quantity of silica dissolved in these five experiments was 30·30 grains, theory requiring 30·277 grains. The silica being highly hygroscopic was the chief cause of the variation in the numbers obtained; it was (in some of the experiments) cooled and weighed in a stoppered bottle, or in a platinum box (with closely fitting lid)

in which it had been heated. In similar experiments, with 100 and 200 grains of purified fine white sand substituted for the precipitated silica, only 6.05 and 8.5 grains respectively were dissolved; these results, compared with those obtained with the precipitated silica, show that unless the silica is very finely divided, much hydrofluoric acid is apt to escape without acting upon it.

From the results obtained with the precipitated silica I conclude: (1st) that the whole of the fluorine contained in the salt is evolved as tetrafluoride of silicon, SiF_4 , and not any as hydrofluosilicic acid, notwithstanding the presence of water formed by the reaction, or even of a limited amount of water added, as in the fifth experiment; and (2nd) that an equivalent, or 78.13 parts, of the dry salt contains two equivalents, or 38 parts, of fluorine; and therefore from these results, combined with the amount of potassium found as chloride in the foregoing determination, I conclude that the salt cannot contain more than a very minute amount, if any, of oxygen or water.

I also checked the foregoing results by various methods of chemical analysis of the anhydrous acid (*see* Phil. Trans. Roy. Soc., 1869, page 177).

One method I employed for analysing the anhydrous acid was as follows:—A six-ounce platinum bottle had a vertical open platinum tube about 4 inches (= 10.2 centimetres) high cemented into its mouth, the tube being perfectly closed by a well-fitting plug of paraffin. The bottle was placed for a short time in a thin tin case immersed in a freezing mixture, then taken out and weighed, and returned to the chilling-case; a small quantity of the acid, not exceeding 50 grains, was then poured into it through a long-necked platinum funnel, the plug fixed securely, and the whole re-weighed. The bottle was now placed in the freezing-mixture, itself at a temperature not above zero, and distilled water added to it in minute drops, at long intervals at first, until about a quarter or half an ounce had been added, taking great care not to cause an escape of vapour. A quantity of hydrate of potash, more than sufficient to convert all the acid into fluoride of potassium, was now dissolved in a separate vessel, and the solution chilled; some of this liquid, more highly diluted, was added in drops to the dilute acid, at intervals at first, and gradually the whole, taking care to cause no escape of vapour. The mixture (of strong alkaline

reaction) was washed into a platinum beaker, and gradually evaporated until a film formed upon it. Precipitated silica, quite dry and perfectly pure, and especially free from matters soluble in hot concentrated sulphuric acid, was weighed in a stoppered bottle in more than sufficient quantity to convert the whole of the fluorine of the acid into tetrafluoride, the contents of the bottle added to the alkaline pasty liquid, and the bottle at once closed and re-weighed. The mixture of silica and alkaline fluoride was incorporated by stirring, and an excess of concentrated sulphuric acid added gradually to it, and the mixture then heated until it was a thin liquid, and the sulphuric acid freely volatilized. The residuary mixture was then dissolved, transferred to a filter, and the silica washed, dried, ignited, transferred to a stoppered bottle, and weighed. This method gave *nearly* accurate results.

The best method of analysis, however, consists in diluting the chilled acid with extreme care, and adding to it very gradually a known weight of pure caustic lime, and weighing the dried and ignited product; the following are the particulars of the process. A six-ounce platinum bottle, provided with a neck about $2\frac{1}{2}$ inches ($= 6.4$ centimetres) high, and $\frac{1}{2}$ an inch ($= 1.3$ centimetre) in diameter, with a flanged mouth, plate with paraffin layer (see page 370) and clamp screws, and previously weighed, was placed in a closely fitting tin case immersed in the freezing mixture of ice and chloride of calcium (see page 369), and about 30 to 50 grains of the acid from a chilled and similar platinum bottle transferred to it. The bottle was then securely closed, removed from its case, and allowed to return to the atmospheric temperature and re-weighed; it was now re-immersed in the freezing-mixture, and when quite cold the plate and screws were removed and *minute portions* of distilled water were allowed to drip down the inner side of the tube until the acid was sufficiently diluted to be able to add gradually in the whole about $\frac{1}{2}$ an ounce of water. Pure caustic lime (which had been repeatedly heated to whiteness until it ceased to lose weight), more than sufficient in quantity to neutralize all the hydrofluoric acid present, was now intensely heated in a small platinum box, and cooled with the lid (a closely fitting one) upon it, and weighed; the whole of the lime was then very gradually added to the dilute acid with shaking, and the mixture digested, with shaking and heating, until the liquid be-

came alkaline to test-paper. On first heating, much heat spontaneously developed itself in the mixture, and required to be moderated by immersing the bottle in cold water, and *after* this development of heat the liquid was alkaline. The mixture was now evaporated and dried in the platinum bottle, then repeatedly ignited to redness and cooled until it ceased to lose weight, and finally weighed, every 22 grains increase of weight being estimated to represent 40 grains of HF present. By these means the loss of acid vapour did not exceed 0.05 grain; the residue was alkaline to test-paper, and the gain of weight found was 55 parts for every 100 parts of liquid acid taken. The following are the numbers experimentally found:—in the first reliable experiment 31.61 grains of the acid and 54.56 grains of lime were taken, and the weight of ignited residue found was 71.93 grains = a gain of 17.37 grains = 31.58 grains of HF present = 99.90 per cent. of HF in the acid. In another experiment 50.26 grains of the acid and 77.54 grains of lime were taken, and the weight of ignited residue was 105.18 grains = a gain of 27.64 grains = 50.27 grains of HF = 100.01 per cent. of HF.

In an analysis by the above process of a portion of non-rectified acid obtained from some double fluoride of hydrogen and potassium which had not been sufficiently fused, and which, from the weight of acid obtained from a given quantity of the salt was suspected to contain traces of the double salt and a small quantity of water, not exceeding at the utmost 3.47 per cent. (see p. 373), 39.39 grains of the acid + 66.74 grains of lime gave 87.78 grains of ignited residue = a gain of 21.04 grains = 38.25 grains of HF = 97.09 per cent. of HF present. These results confirm all the former ones, and further support the conclusion that the liquid obtained by distilling properly prepared fluoride of hydrogen and potassium, and rectifying the product at a temperature not exceeding 100° F., is anhydrous hydrofluoric acid. The lime for the above process was prepared as follows: an excess of clear lime-water was added to a solution of nitrate of calcium; the filtered solution precipitated by a mixture of solution of ammonia and sesquicarbonate of ammonium; and the precipitate was washed and dried, and repeatedly ignited to an incipient white heat in an open platinum crucible in a small gas furnace. The presence of magnesia in the lime does not affect the numerical relation of the gain of weight to the

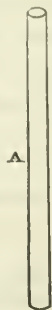
amount of acid present. Various attempts were made to employ pure oxide of magnesium in place of the lime, but its power of neutralizing the acid was found to be too slow.

Molecular Volume of the Anhydrous Acid in the gaseous state.

I have made fourteen separate attempts to ascertain the volume of gaseous product formed by the chemical union of one volume of hydrogen with fluorine. The method I have adopted has been to heat pure anhydrous fluoride of silver to fusion in a platinum vessel containing an equivalent quantity of pure and dry hydrogen. The experiments were extremely difficult, owing to the destructive nature of the substances, and the consequent difficulty of eliminating the numerous interferences which presented themselves. The following are the particulars of the method finally employed. Fragments of the purest magnesium were introduced into the neck of an inverted bottle full of previously boiled and partly cooled dilute sulphuric acid, consisting of one measure of the purest acid, and about forty or fifty of distilled water. The mixture was stirred with a rod of magnesium immediately before use. When the bottle was quite full of hydrogen, the gas was transferred to a dry bottle filled with mercury and inverted over mercury; sticks of hydrate of potash were then agitated occasionally with the gas at intervals during several hours, and the gas transferred to a graduated tube over mercury, and allowed to remain in contact with sticks of dry phosphorus during twelve hours, the phosphorus being used to remove oxygen introduced by traces of air adhering to the vessel, &c.

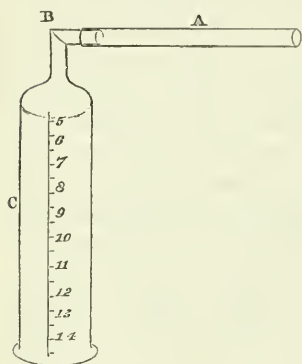
About 15.3 grains of fluoride of silver of a very high degree of purity (made from pure materials, viz., hydrofluoric acid and carbonate of silver) was placed in the previously heated and weighed platinum tube A (fig. 5), which was open at the top and closed at the bottom, and constructed without solder by the process of melting. The tube was $6\frac{1}{2}$ inches (= 16.6 centims.) long and $\frac{13}{16}$ of an inch (= 2.1 centims.) diameter, and had a capacity of 3.4 cub. inches (= 55.716 cub. centimetres); in some of the experiments, where accurate weighing was not required, it was coated externally for about 2 inches

Fig. 5.



(= 5.0 centims.) in length at its closed end with a thick layer of copper by the electrolytic process; the object of coating it thus was to prevent traces of hydrogen passing through the platinum at a red heat; this may, however, be dispensed with by not applying more than a barely visible red heat in the subsequent reduction part of the process. The fluoride was now melted in it at a visible red heat until it formed a tranquil liquid, and the

Fig. 6.



upper part of the tube also heated to redness to expel all moisture.*

The tube was then either at once affixed to the platinum receiver (see fig. 6), or as soon as possible corked, cooled, and re-weighed; the loss of weight upon the above quantity of salt was usually 0.1 grain, arising from moisture expelled from the fluoride (which is a very hygroscopic and deliquescent substance), and partly from the moisture of the air decomposing a little of the fluoride during the fusion. The tube A

was now fixed tightly upon the open bent platinum neck-tube B of the graduated platinum receiver C, and the junction made perfectly gas-tight by a small quantity of the melted mixture of sulphur and lamp-black, bound over tightly by a stretched ribbon of the thinnest vulcanized india-rubber, secured by string. The platinum receiver, C, was 6 inches (= 15.3 centims.) long and $1\frac{1}{2}$ inch (= 3.8 centims.) diameter, open and flanged at the bottom end and formed in one piece with the bent neck B without solder. Glass receivers were found to be corroded even when thickly and carefully coated with paraffin. (N.B. They were used before I succeeded in obtaining the hydrofluoric acid in a perfectly anhydrous state.) They might perhaps be used provided moisture is perfectly excluded and the acid is *not allowed to assume the liquid state*. The entire apparatus, including A, B, and C, when put together had a capacity of about 15 cub. inches (= 245.805 cub. centims.).

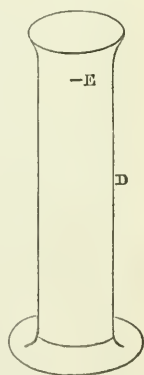
The tubes A and B were now filled as quickly as possible

* Oxide of silver was found to be decomposed at a temperature much below that of visible redness. H. Rose states that Ag_2O begins to evolve oxygen at 250°C . Watts's Dictionary of Chemistry, vol. i, p. 792).

with dry mercury, and tapped persistently to remove any adhering bubbles of air; the receiver C was then also similarly filled and tapped, and inverted over mercury in a large mercurial trough. 5.5 cub. inches (= 90.128 cub. centims.) of the prepared hydrogen which had lain many hours in the measuring-tube in contact with the phosphorus was now transferred to the platinum apparatus, and the tube A inclined and persistently tapped, so as to shake out of it as perfectly as possible all the mercury. A stick of dry phosphorus was again placed in the gas for one hour to remove any oxygen introduced by adhering air bubbles, or by air lodging in the crevice at the junction of the two tubes.

The apparatus and its contents were next removed from the mercurial trough by means of the glass vessel D, which was about 8 inches high (= 20.4 centims.) and 2 inches (= 5.1 centims.) in diameter, and were supported within this vessel by mercury at such a height that the figure "5.5 CI" of the graduation upon the platinum-receiver coincided in horizontal position with the mark — (shown at E, Fig. 7) near the top of the outer vessel. Additional mercury was now poured into the outer vessel until it attained this same indicated level at the atmospheric temperature, and was therefore at the same level inside and outside the platinum-receiver. The tube A being supported horizontally, a wet rag was now laid upon it near the sealed junction, and heat applied gently to the outer end by means of a spirit-lamp until a barely visible redness was attained, this being quite sufficient to melt the enclosed fluoride of silver. This degree of heat was maintained about one hour, and near the termination of the heating process a much higher and variable temperature was applied for a short time, but not sufficiently high to melt the reduced silver. The mercury in the outer vessel was kept at the original level during the heating process, &c., by raising or lowering the platinum apparatus as occasion required. The whole apparatus was then placed in a suitable air-bath, and gradually heated to a uniform and constant temperature of about 212° F. (= 100° C.), a thermometer being placed in the vessel of mercury D, and another near it in the air-bath. The platinum apparatus was raised gradually as

Fig. 7.



the gas expanded, to keep the mercury at the original level, and the volume of enclosed gas was noted at the various temperatures.

In each instance, during the decomposition of the silver-salt by the hydrogen, after the first expansion (produced by the heat) a very large *reduction* of volume occurred; for instance, 10.0 cub. inches (= 163.87 cub. centims.) were reduced to 6.5 (= 106.5 cub. centims.); and on removing the lamp and allowing the whole apparatus to cool to 50 or 60° F. (= 10° to 15°·5 C.), a still further and very large contraction invariably occurred; for instance, 6.5 cub. inches (= 106.5 cub. centims.) became 3.0 cub. inches (= 49.161 cub. centims.), even while under a rarefaction of 5 inches (= 12.75 centims.) height of mercury. Similar contractions to very small volumes at the atmospheric temperature took place in all the experiments. These reductions of volume were in the earlier trials somewhat due to small quantities of air present, the oxygen of which formed water with some of the heated hydrogen and condensed a little of the acid vapour. In all cases, however, the contraction of volume was evidently nearly wholly due to the partial condensation of the hydrofluoric-acid vapour within the vessel to a liquid state. This liquid could not of course be seen, on account of the opacity of the apparatus, and being very minute in amount (probably less than half a drop for each cubic inch (= 16.387 cub. centims.) of hydrogen employed) and very volatile, it was in all cases instantly converted into a dense fume on opening the vessel. The mere warmth of the hand was sufficient to make the partly liquefied acid expand very greatly. These results of contraction agree with and confirm the results already found in my experiments, viz., that anhydrous hydrofluoric acid is a very volatile liquid at 60° F.

The following are the actual results obtained in one of the first reliable approximate experiments. Six cub. inches (= 98.322 cub. centims.) of prepared hydrogen at 50° F. and 16.4 grains of fused fluoride were employed. During the first three minutes of heating the gas expanded to 7.8 cub. inches (= 127.8 cub. centims.). Contraction then commenced and continued during about twenty-five minutes, the volume being gradually reduced to about $4\frac{1}{2}$ cub. inches (= 73.74 cub. centims.). The heat was continued about half an hour longer, and the apparatus then, whilst still warm, placed in the air-

bath, and heated gradually to a fixed temperature of 200°F. ; the volume of gas was then 14.5 cub. inches ($= 237.61$ cub. centims.) $= 11.2$ cub. inches ($= 183.53$ cub. centims.) at 50°F. The rate of expansion was somewhat greater at the higher degrees of temperature than at the lower ones; for instance, at 139°F. the volume was 12.1 cub. inches, at 160°F. 12.85, at 186°F. 14.0. Only a minute quantity of undecomposed silver fluoride was found after the experiment.

In another experiment, with 5.5 cub. inches ($= 90.128$ cub. centims.) of hydrogen at 50°F. and standard pressure, and 15.3 grains of fluoride, on applying heat the gas expanded to 7.3 cub. inches ($= 119.625$ cub. centims.) at the end of three minutes; it then gradually contracted during the next twenty minutes to about 4.2 cub. inches ($= 68.825$ cub. centims.); the heat was continued about twenty minutes longer with occasional heating to full redness (but not sufficient to fuse the enclosed reduced silver). The apparatus was then at once transferred to the hot air-bath, and heated gradually to 212°F. , and kept at that temperature some time. The volume of gas thus found was 12.8 cubic inches ($= 209.75$ cub. centims.) at 176°F. , 13.0 ($= 213.03$ cub. centims.) at 184°F. , and 14.0 ($= 229.418$ cub. centims.) at 212°F. ; the latter number, after correction for the amount of displacement of the level of the mercury by the thickness of the sides of the platinum vessel between "5.5," the original depth of immersion, and "14," the final one, was 14.3 ($= 234.33$ cub. centims.); this is equal to 10.84 cub. inches ($= 177.635$ cub. centims.) at 50°F. , the theoretic quantity required being 11.0 inches ($= 180.257$ cub. centims.). On cooling the apparatus to 50°F. , the mercury rose and filled the platinum tube to within about 0.7 cub. inch ($= 11.77$ cub. centims.) of its capacity, even whilst under rarefaction by a column of mercury about 3.5 inches ($= 8.9$ centims.) in height. Minute traces only of undecomposed fluoride of silver were found in the tube after the experiment.

From the results obtained, it appears that one volume of hydrogen in uniting with fluorine, produces not simply one volume of gaseous product as it does when uniting with oxygen, but two volumes, as in the case of its union with chlorine.

According to M. Prat* anhydrous fluoride of silver contains

* Comptes Rendus, No. 9, August, 1867.

oxygen, its constitution being 1 equiv. of fluorine = 29·6, 1 equiv. of oxygen = 8, and 2 equivs. of silver = 216. The results obtained in these experiments contradict this view; for according to it the volume of gases obtained should have been less, as 1 volume of hydrogen in uniting with oxygen produces only 1 volume of gaseous product.

To obtain a numerical result more nearly approaching theoretical accuracy than in the foregoing experiments, various minute corrections would have to be applied:—1st, for the increased capacity of the platinum apparatus caused by its expansion by heat; 2nd, for the rise of level of the mercury caused by its expansion by rise of temperature; 3rd, for the lowering of the said level by expansion of the glass containing-vessel; 4th, for the rise of the said level caused by the immersed bulb of the thermometer; 5th, for the variation of atmospheric pressure during the experiment; and 6th, for the meniscus, &c.

To ascertain the loss of weight by the fluoride of silver in the preceding experiments, 12·8 grains were put into a platinum boat enclosed in a roll of platinum-foil, and heated to tranquil fusion at a gentle red heat in a platinum tube-retort (similar to the tube A in fig. 5), then cooled and weighed; the loss was 0·10 grain. The boat and foil were now put into a long horizontal platinum tube and gently heated in a slow current of hydrogen (which had been generated by magnesium and pure dilute sulphuric acid, and dried by two wash-bottles of strong sulphuric acid), the current of gas and the heat being maintained until acid fumes entirely ceased; the loss of weight was 1·80 grain. This is less than the theoretic quantity by 0·10 grain, which is partly (if not wholly) accounted for by the fact that fluoride of silver, even when carefully prepared from pure materials, is liable to contain a variable amount of metallic silver, which is left as an insoluble black powder on dissolving the salt in water. This free silver is formed in the process of drying the salt, by the aqueous vapour from the imperfectly dried portions and from the surrounding air decomposing the dry and hotter portions; it is increased in quantity every time the salt is fused in contact with atmospheric air.

[To determine the amount of silver in the fluoride, 15·89 grains of perfectly anhydrous fluoride was dissolved in water, the solution filtered, the separated black precipitate washed,

and the silver in the filtrate determined by addition of chloride of potassium; it gave 18.00 grains of chloride = 13.55 grains of silver. The black matter weighed 0.1 grain after ignition; deducting this amount, the 15.79 grains of fluoride contained 13.55 grains of silver: theory requires 13.437 grains. On several occasions I have had reason to suspect a slight degree of solubility of the separated and finely divided metallic silver in a strong aqueous solution of silver fluoride, similar to that of lead and silver in strong aqueous solutions of their respective nitrates; and if this be correct it may account for the slight excess of silver found in this determination. The amount of fluorine in the filtrate was determined by means of a solution of calcium salt in the usual manner; it gave 4.40 grains of fluoride of calcium = 2.1436 grains of fluorine, the quantity required to complete the weight being 2.24 grains. In my hands this process of determining the amount of fluorine has not hitherto yielded very accurate results.—Received January 9, 1869.]*

These results, combined with the foregoing experiments on molecular volume, agree with the conclusion that a volume of hydrogen weighing 1 unites with 19 parts by weight of fluorine to form 2 volumes of hydrofluoric acid, and that the specific gravity of gaseous anhydrous hydrofluoric acid is ten times the amount of that of hydrogen.

The acid vapour obtained by heating fluoride of silver in the closed vessel of hydrogen over mercury, as already described, was transferred to glass vessels over mercury; it was colourless, and quite transparent; it did not corrode the glass vessels or render them dim in the slightest degree during several weeks, provided moisture was entirely absent; but if there was the slightest trace of damp present the surface of the glass soon lost its brightness. A fragment of ice introduced into the gas instantly caused the surface of the glass near it to become corroded and opaque white. The vapour of hydrofluoric acid escaping at any minute orifice from a vessel of the dry acid, condenses moisture rapidly upon the contiguous parts of the vessel.

Fremy sought for oxygen in the anhydrous acid, but was

* Note, added May 25, 1869. I have since, by repeated and more accurate analyses, confirmed the composition of the recently fused salt to be wholly silver and fluorine, with a small quantity of enclosed metallic silver.—G. G.

unable to find any*. Sir H. Davy also, who prepared his acid by distilling fluor-spar with sulphuric acid containing not more than 1 equivalent of water, could find no oxygen in it, either by electrolysis, or by neutralizing it with gaseous ammonia; but when the sulphuric acid he employed contained more than 1 equivalent of water, he found water in the hydrofluoric acid. The acid obtained in my experiments also I consider to be destitute of oxygen, not only from the results obtained in the various analyses and experiments already described, but also, 1st, because the double fluoride of hydrogen and potassium from which the acid was prepared, when fused and electrolyzed with platinum electrodes, evolved abundance of inflammable gas at the cathode, but yielded no gas at the anode, although oxides are by electrolysis decomposed before fluorides; 2nd, the electrolysis of the anhydrous acid with platinum electrodes yielded no odour of ozone, whereas hydrofluoric acid containing various percentages of water evolved that odour strongly (see pages 404 and 405); 3rd, the properties of hydrofluoric acid prepared by heating pure fluoride of silver in pure hydrogen (see page 380) agreed in properties, as far as those properties were ascertained, with the acid obtained from the double salt; and 4th, because two volumes of gaseous anhydrous hydrofluoric acid were produced by the reaction of one volume of hydrogen upon its equivalent of fluoride of silver, whereas if oxygen had been present, less than two volumes of acid gas would have been produced. All the results also support the conclusion that the acid obtained by heat from the double fluoride, and that from pure fluor-spar and mono-hydrated sulphuric acid heated together in a platinum retort, is free from oxygen and water. The complete synthesis of the acid can only of course be performed by means of hydrogen and free fluorine.

To determine the specific gravity of the anhydrous acid, I employed a thin platinum bottle of the form and size of the annexed sketch (fig. 8); with the stopper in its place the bottle contained 1000 grains of distilled water at 60° F. The stopper had a minute tube up its centre, and also two funnel-shaped cavities, one at each end, as shown in the sketch. A thin platinum wire was also soldered round the stopper to form a shoulder, which rested upon the neck of the bottle when the

* Comptes Rendus, February 27th, 1854.

stopper was tightly down in its place. A specific-gravity bottle made of gutta-percha would not resist the action of the acid.

Fig. 8.

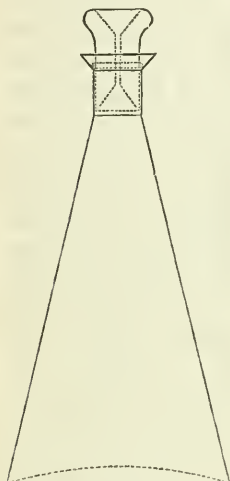
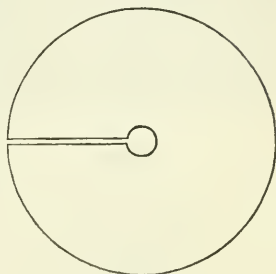


Fig. 9.



Fig. 10.

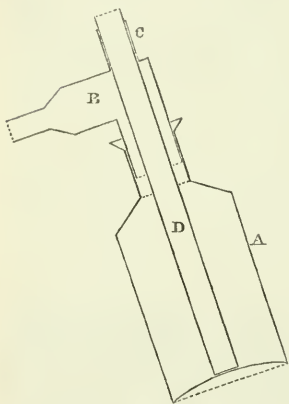


Sponge was employed to absorb the excess of acid around the stopper. The specific gravity found of the pure rectified acid in two separate experiments was 0.9885 at 56° 5 F., that of water being = 1000; whilst that of a less pure sample was 1.036 at 60° F. (Sir H. Davy found 1.0609). These results are not perfectly accurate, owing to the unavoidable escape of acid vapour, but the amount of error is probably not more than 1 part in 1000. The specific gravity of the pure rectified acid was also found by weighing a platinum tube (which had been previously filled with paraffin by fusion) separately in the acid and in distilled water, both at 52° F.; the number found was 0.9922, assuming that of water to be = 1000 at 52° F. By weighing a closed platinum vessel of the annexed size and form (fig. 9) separately in the acid and in distilled water, both at 55° F., the specific gravity found was as 0.9879 is to 1.0000; this result is the most accurate one obtained: the pure acid is therefore a little lighter than water. The vessel containing the acid was covered by a thin plate of paraffin of the annexed form (fig. 10) during the weighing.

The acid obtained in my experiments was much more volatile

than sulphuric ether. I ascertained its boiling-point as follows. A platinum bottle, A (fig. 11), of about $2\frac{1}{2}$ ounces' capacity, had a platinum angle-tube, B, which fitted tightly into its neck; the angle-tube had a short open tube, C, within which a platinum tube, D, was tightly fitted and luted with the melted sulphur mixture (see page 369); this tube was open at its upper end and closed at its lower end, and was for the purpose of receiving a thermometer.

Fig. 11.



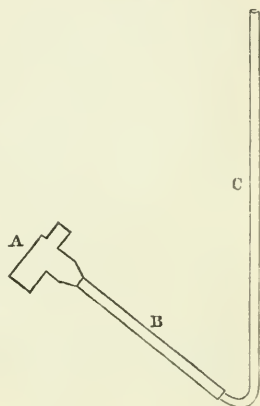
About two ounces of the perfectly pure and previously chilled acid was poured into the chilled bottle A, the angle-tube inserted and luted securely with paraffin, the smaller end of the angle-tube fixed within the platinum tube of a Liebig's condenser (with freezing-mixture, see page 369) and luted with the paraffin mixture. A platinum bottle was affixed to the condenser to receive the distillate. The bottle was now immersed in a small water-bath, a thermometer placed in the water, another within the tube in the acid, and heat very gradually applied to the water. The acid boiled at 67° F., the mercury of the inner thermometer remaining

stationary at that point, and that of the outer one at about 77° F., until nearly all the acid had passed over. By applying a stethoscope to the end of the inner tube D, the boiling could be feebly but distinctly heard; a slight escape of fume at the exit-tube of the receiving-bottle (see page 370) commenced with the boiling, continued with it, and ceased when the boiling ceased. At -30° F. ($= -34\frac{1}{2}^{\circ}$ C.) the acid is still a perfectly mobile liquid, fuming but little in a narrow-necked bottle, and its solidifying point is probably very many degrees below this (see also page 403).

The vapour-tension of the acid at 60° F. is very considerable, and an experiment was made in the following manner to determine approximately the degree of pressure to which the bottles containing the acid were subjected at ordinary temperatures. A six-ounce platinum bottle containing between four and five ounces of the anhydrous and pure acid in a chilled

state was connected air-tight, by means of the platinum angle-tube A (fig. 12), with an inclined platinum tube B, about 16 inches ($= 41.7$ centims.) long and $\frac{3}{8}$ of an inch ($= 0.95$ centim.) diameter, and a vertical bent and open glass tube C^t about 30 inches ($= 76.25$ centims.) high and $\frac{1}{8}$ of an inch ($= 0.32$ centim.) bore, the bent portion of the tubes being filled to about 6 inches ($= 15.3$ centims.) in height with mercury. The bottle was now gradually allowed to attain a temperature of 60° F. At that temperature the difference of level of the mercury in the two tubes was $15\frac{1}{2}$ inches ($= 39.4$ centims.), and therefore the pressure upon the interior of the bottle was $= 7.58$ pounds per square inch. No leakage occurred at the cemented

Fig. 12.



joints. The results of this experiment, together with those of the previous ones, show the necessity of keeping the acid in a cool place. On loosening the lid of a bottle of the acid at 60° F., the acid vapour is expelled in a jet, like steam from a boiler.

The low boiling point, the extremely dangerous and corrosive nature of the acid, and its great affinity for water, illustrate the very great difficulty of manipulating with it and retaining it in a pure state; nevertheless, by the contrivance described (see page 371), and placing the bottles containing it in a cool cellar (never above a temperature of 60° F.), the author has succeeded in keeping the liquid acid perfectly, without loss, and unaltered through the whole of the recent hot summer.

The following is the order of electrical relation found with different metals, &c., in the pure anhydrous acid at 0° F.:—zinc, tin, lead, cadmium, indium, magnesium, cobalt, aluminium, iron, nickel, bismuth, thallium, copper, iridium, silver, gas-carbon, gold, platinum, palladium. The acid in these experiments was contained in a covered deep and narrow platinum cup placed in a tin chilling case immersed deeply in the freezing-mixture.

Sir H. Davy electrolysed the liquid acid prepared by distilling fluor-spar with strong sulphuric acid. He cemented a

platinum wire by fusion into a cup of horn silver, and inverted the cup in the acid in a tray of platinum. He used a very weak voltaic current, and kept the apparatus cool by a freezing mixture. The platinum wire rapidly corroded and became covered with a chocolate-coloured powder. Inflammable gas like hydrogen was evolved from the cathode. He also tried a plumbago anode, but it was quickly destroyed, and the liquid became turbid and black; also a charcoal anode upon the end of a platinum wire; the charcoal absorbed the acid, and made the platinum wire the pole.* G. J. Knox† also electrolysed hydrofluoric acid with a charcoal anode attached to a platinum wire, and a platinum wire cathode, in a vessel of fluor-spar half filled with the acid, and having a perforated stopper of the same spar dipping into the acid. It is not stated in the above paper how the acid was prepared or its purity determined, nor by what means charcoal capable of resisting the acid was obtained.

I have made numerous experiments of electrolysing the pure anhydrous acid with various electrodes. The method adopted in many of the experiments was to place a platinum cup about $3\frac{1}{2}$ inches (= 9 centims.) deep and $1\frac{3}{4}$ inch (= 4.5 centims.) wide in a tin case (weighted with lead) in the freezing-mixture; the cup was about half filled with the acid, and was closed by a well-fitting stopper of paraffin, through the centre of which a long rod or plate of the substance constituting the anode was closely fixed, the cup itself being the cathode; a loosely fitting cup of paraffin about half an inch deep, and provided with a handle, was immersed in the acid beneath the anode to collect particles which fell from the anode, and to prevent hydrogen ascending from the bottom of the platinum vessel and coming into contact with the positive electrode. The following are some of the results obtained. The liquid acid conducted with a platinum anode much more readily than pure water; with four Smee's elements it began to conduct visibly, and with ten elements it conducted readily. No odour of ozone was evolved, and the platinum anode gradually acquired a thick red-brown crust. By employing forty Smee's elements the conduction was copious; the anode rapidly corroded, and much finely divided platinum as a greyish-black

* Works of Sir H. Davy, vol. v, p. 416.

† Philosophical Magazine, 3rd series, vol. xvi, p. 192.

powder collected in and beneath the paraffin cup; this powder appeared to be due to detached particles of the red-brown crust becoming reduced by the diffused bubbles of free hydrogen from the cathode, or was composed of particles of metal mechanically detached from the anode by the current. Portions of the soft earthy crust were scraped off at intervals into a platinum dish upon a heated slab of iron; it dried to a dark-brown earthy salt (doubtless fluoride of platinum) which rapidly deliquesced in the air to a tenacious sticky mass, similar to damp fluoride of silver; the anhydrous platinum compound was perfectly insoluble in the acid, but formed a blood-red liquid (like a solution of tetrachloride of platinum) with cold water, and the dilute aqueous solution, when heated, became full of flocks by separation of an insoluble basic salt. By far the greater portion of the platinum compound detached itself from the anode and became reduced to the metallic state, and only a small amount was left upon the anode as a soluble salt. The whole of the powder in the paraffin cup was found by appropriate tests to be metallic platinum. With an anode of very close-grained gas-carbon and six Smee's elements, conduction occurred freely, and in less than half an hour nearly half the thickness of the carbon rod was disintegrated and fell as a loose powder to the bottom of the vessel. Numerous attempts were made to electrolyse the acid with a charcoal anode; fifteen different kinds of wood, including some of the densest kinds, were converted into charcoal by very gradual drying and equally gradual heating to full redness in a copper tube retort until all evolution of gas ceased. Some of the resulting rods were exceedingly hard and dense, and emitted a clear metallic ringing sound when struck; the denser kinds, especially those free from cracks, conducted freely even with ten Smee's elements. The best kinds were those made from kingwood, beech, ebony, lignum-vitæ, and boxwood; that from lignum-vitæ was nearly as hard as baked earthenware.* On immersing either of the rods in the acid, even without passing an electric current, it soon began to crack and fly to pieces, and on passing the current, the rods commenced breaking immediately, and in some instances with dangerous violence, projecting fragments to a considerable distance; even the hardest

* For the preparation of articles and vessels of charcoal for these experiments, see Philosophical Magazine, September, 1868.

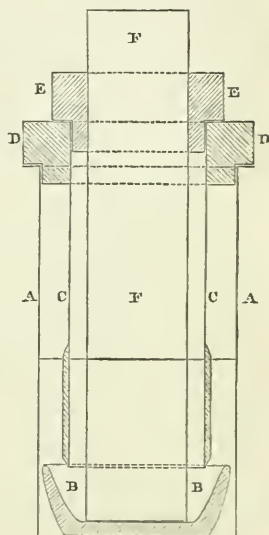
and densest kinds of charcoal behaved thus and became brittle throughout the immersed parts; the most resisting kind was that made from beechwood. The number of Smee's elements employed varied from ten to fifty-six, and the kind of electrolysis-cell used was that represented by Fig. 13 (see page 391). The cracking of the charcoal was attended by evolution of numerous bubbles of gas (probably air previously absorbed by the carbon); on this account, and also in consequence of the fume developed by the heat of conduction-resistance in the charcoal, it was difficult to ascertain if the anode evolved gas due to electrolysis; nevertheless, with the aid of a strong light and watching for opportunities, it was found that the passage of the current was *not* attended by any distinct increase of gas from the anode. No special odour could be detected above the anodes, but on removing the charcoal from the liquid it evolved a feeble odour somewhat like that of chlorine, in addition to the intense one of the acid. The kinds of wood employed for making the charcoal were beech, kingwood, ebony, lignum-vitæ, box, mahogany, zebra, Memel oak, English oak, rosewood, maple, lancewood, walnut, Norwegian pine, and ironwood. The fracture of the carbons was not caused by the lowness of the temperature of the acid.

With an anode of pure sheet gold the acid scarcely conducted at all, except for a short time, even with forty Smee's elements; by continuing the action about $1\frac{1}{2}$ hour, the anode acquired a dark reddish-brown film and a few crystals upon its edges, which were at first of a green colour, but became red by exposure to the air. With a palladium anode the acid conducted somewhat less freely than with one of platinum or gas-carbon; and by employing forty Smee's elements the palladium anode was also corroded. The salts which fall off the anodes appear to be wholly converted into metal by the disseminated minute bubbles of hydrogen, and even some of the coating of the anode itself is partly so converted if the hydrogen is allowed to come into contact with it. The action in the electrolysis-cell was sometimes watched by the aid of a magnesium light, as the fume was usually too dense to admit of inspection by ordinary light.

The most effective form of electrolytic apparatus employed is represented by the annexed figure. AA is a circular and deep platinum cup; BB is a shallow and loosely fitting cup of

paraffin provided with a handle (not shown); CC is a wide tube of platinum, open at both ends, and fixed at its upper end within an equally wide circular pre-foration in the annular paraffin stopper, DD; EE is an inner stopper of paraffin fitting within the other, and supporting a sheet of platinum or other metal, FF, which passes through it and constitutes the anode. The use of the tube CC is to prevent the hydrogen evolved at the inner surface of the cathode, AA, coming into contact with the anode, F. The tube CC is coated on its outer side at its lower end and up to a short distance above the level of the liquid with a thin layer of paraffin, to prevent the tendency of electrolytic action upon it. Electrolysis tends to first decompose any traces of water the acid may contain, and thus maintain the acid in an anhydrous state.

Fig. 13.



Two ounces of strong sulphuric acid was added to a mixture of 336 grains of pure fluoride of sodium and 472.5 grains of nitrate of potassium, both in fine powder, in a platinum retort, the mixture distilled, and the product received in a platinum bottle. The distillate weighed 678.2 grains, it should have weighed only 664 grains; the excess was probably water, from the sulphuric acid not being of maximum strength. In applying the heat, the retort was immersed in a bath of linseed-oil, the temperature of which was not raised above 450° F. No permanent gas was evolved during the process. The product was a colourless fuming liquid, much less fuming than anhydrous hydrofluoric acid, and did not corrode paraffin or platinum, but corroded vulcanized india-rubber rapidly. This liquid was electrolysed by means of six Smee's elements and two large platinum electrodes, during five hours, the liquid being in a covered narrow and deep platinum cup immersed in a freezing-mixture; conduction occurred freely, and an odourless gas (doubtless ordinary oxygen) was freely evolved from the anode;

the anode was not corroded, and both electrodes were unaltered in weight.

520 grains of anhydrous hydrofluoric acid was distilled from about 2000 grains of KF , HF in a platinum retort through a platinum tube surrounded by the freezing mixture into a platinum bottle (surrounded by the same mixture) containing 334.17 grains of fibrous sulphuric anhydride; the first contact of the two substances was attended by a hissing sound and evolution of great heat, and the resulting compound was a colourless liquid, of a less fuming character than either of the two substances alone. In this experiment it was necessary to cement the junctions near the receiver with the melted sulphur mixture (see p. 369), as paraffin is rapidly blackened by the vapours of sulphuric anhydride*. The compound formed in this case was probably analogous in some respects to partially hydrated sulphuric acid, 2HF taking the place of H_2O , and corresponds to the third hydrate of sulphuric acid, or $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$. This liquid was also electrolyzed by means of platinum electrodes and ten Smee's elements; the conduction was moderate (less than with HF alone), and the anode was corroded. Sulphuric anhydride added to the mixture produced heat.

To obtain an idea of the *general* chemical behaviour of the pure anhydrous acid, numerous substances (generally anhydrous) were immersed in separate portions of it in platinum cups, contained in a tin chilling-case sunk deep in the freezing-mixture (see p. 369), and sometimes covered with plates of transparent fluor-spar;† the temperature of the acid varied from 20° to 0° F. It slightly dissolved bromine to a liquid of an orange colour; iodine, carbon, boron, silicon, sulphur, selenium, tellurium (in powder), and phosphorus were unchanged. The noble and base metals were unaffected; and even magnesium, aluminium, zinc, cadmium, tin, lead, reduced iron, arsenic, antimony, and bismuth in a state of fine powder did not cause any evolution of hydrogen. Sodium and potassium behaved much the same as with water, the latter producing vivid combustion. Nearly all the salts of the alkali and alkaline-earth metals produced strong chemical action. The acid produced violent

* Gun-cotton inflamed by contact with sulphuric anhydride.

† I have obtained suitable vessels, plates, and stoppers of fluor-spar of Mr. J. Tym, Speedwell Mine, Castleton, Derbyshire.

chemical action with the following anhydrides:—Fused boracic, silicic (only when in fine precipitated powder, not with small granules of quartz or even with fine white sand), sulphuric, phosphoric, molybdic, vanadic, and niobic anhydrides; selenious and arsenious anhydrides dissolved freely; antimonious, tungstic, and titanitic anhydrides were either but little or not at all affected nor dissolved; chlorochromic acid would not mix with the acid. With concentrated nitric and sulphuric acids the acid mixed quietly, but with strong hydrochloric acid it produced active effervescence. With lime, baryta, strontia, and the hydrates of soda and potash it united powerfully, and with magnesia less strongly. No effect occurred with the peroxides of silver, iron, lead, thallium, or manganese; nor with the suboxide or protoxide of copper, the oxides of nickel, cobalt, tin (both oxides), or cerium. Teroxide of antimony, bismuth, and the oxides of silver, glucinum, and lanthanum produced strong chemical action, but did not dissolve. The oxides of mercury (both) and lead (both) were changed to fluorides, and apparently also were oxide of zinc and peroxide of barium, the latter with most violent action (probably water was present). Binoxide of platinum was slightly dissolved, and the oxides of uranium and chromium freely; chemical changes also occurred with the lower oxides of vanadium and titanium, and with alumina. The nitrates of lead, uranium, strontium, and barium exhibited no strong chemical action, and did not dissolve, but signs of free nitric acid appeared; nitrate of silver was unaffected (?); nitrate of potassium dissolved freely with a hissing sound; nitric acid was found, by suitable tests, to be set free with the nitrates of lead, barium, and potassium. The fluorides of antimony, bismuth, mercury, copper, nickel, cobalt, iron, lead, tin (both), cadmium, zinc, manganese, cerium, aluminium, magnesium, and calcium were either slightly or not at all affected, and did not dissolve; the fluorides of uranium and chromium exhibited chemical change and dissolved. Alkaline fluorides were strongly affected; the fluorides of silver, barium, and lithium, also cryolite, hissed strongly but did not dissolve; and those of thallium, strontium, sodium, potassium, rubidium, and ammonium produced different degrees of violent chemical action and solution; the acid fluoride of potassium also produced strong action and solution: the behaviour of the alkaline fluorides with the anhydrous acid may be compared to that of the alkaline

oxides and hydrates with water. Solid terchloride of carbon, and the chlorides of silver, mercury (both), copper, nickel, cobalt, lead, cadmium, manganese, and the violet sesquichloride of chromium were undissolved and unaffected; the liquid tetrachloride of carbon, and the liquid chlorides of sulphur, phosphorus, arsenic, and tin would not mix with the acid, whilst the liquid perchloride of antimony and tetrachloride of titanium were decomposed, with violent action and formation of deliquescent solid residues, as when water is added to them; the solid perchloride of phosphorus was also violently decomposed and a white powder formed; the chlorides of calcium, barium, lithium, sodium, potassium, and ammonium were decomposed, with strong action and effervescence, the latter four with solution and especially strong action. The chlorates of sodium and potassium were rapidly decomposed, with evolution of yellow fumes of peroxide of chlorine; no visible effect occurred with the chlorate of barium or perchlorate of potassium. Terbromide of antimony turned white, as on addition of water, and did not dissolve; the bromides of zinc and cadmium were but little affected; the bromides of calcium, barium, and potassium were decomposed with strong effervescence, and the latter bromide dissolved; bromate of potassium was also rapidly decomposed with copious liberation of bromine. The teriodides of arsenic and antimony, the tetraiodide of platinum, iodide of silver, biniodide of mercury, subiodide of copper, and the iodides of lead, cadmium, and zinc were unaffected, whilst the iodides of calcium, barium, sodium and potassium were strongly decomposed, and iodine freely liberated in the first three instances. Iodate of potassium also exhibited some chemical action, but no iodine was set free. The acid decomposes all carbonates; the anhydrous carbonates of silver, copper, cobalt, lead, cadmium, zinc, manganese, calcium, strontium, barium, lithium, sodium, potassium, and ammonium, were all decomposed, with effervescence; those of the alkali and alkaline-earth metals exhibited violent action. Fused borax and the borate of ammonium produced powerful chemical action. The boro-fluorides of sodium and potassium were unaffected. Glass was rapidly corroded. (N.B. It was not corroded in the *gaseous* acid: see page 383.) The silico-fluorides of sodium and potassium dissolved with effervescence; titano-fluoride of potassium also dissolved with strong action. Carbonic bisulphide would not mix with the

acid; the acid had also no chemical or solvent effect upon the sulphides of arsenic (both), antimony (the black sulphide), palladium, mercury (vermilion), copper (subsulphide), iron (both), lead, tin (the bisulphide), cadmium, zinc, and molybdenum; the sulphides of calcium, barium, sodium, and potassium were violently decomposed with evolution of sulphuretted hydrogen, and in the latter instance with separation of liquid sulphur. Bisulphite of sodium dissolved with effervescence. Sulphate of cobalt was unaffected; the sulphates of calcium, strontium, and barium partly dissolved with a hissing sound; sulphate of sodium and acid sulphate of potassium exhibited strong action and dissolved. Chrome-alum dissolved quietly to a purple liquid, and sulphate of ammonium to a colourless liquid. Phosphide of copper was unaffected; phosphide of calcium was powerfully decomposed; phosphate of copper was also decomposed; phosphate of uranium produced action; phosphate of calcium was partly dissolved, and phosphate of ammonium completely. Arsenite of copper was decomposed; arsenite and arseniate of ammonium, and the arseniate of magnesium and ammonium, produced violent action; the first and third were dissolved. Damp crystals of permanganate of potassium hissed, and dissolved to a deep-green liquid. Red chromate of lead became yellow and partly dissolved; yellow chromate of lead dissolved to a yellow liquid; the mono-chromates of sodium and potassium, and the acid chromates of sodium, potassium, and ammonium dissolved with violent action to blood-red liquids, with evolution of vapour of fluoride of chromium; vanadate and metavanadate of ammonium produced powerful action, the former partly, and the latter wholly dissolving to yellow liquids. Native molybdate of lead was unaffected; molybdate of ammonium produced strong action but did not dissolve. The tungstates of sodium and ammonium were violently decomposed, the former dissolved, and the latter remained insoluble. Cyanide of mercury was partly dissolved; cyanide of potassium was violently decomposed, with liberation of hydrocyanic acid; anhydrous ferrocyanide of potassium dissolved with violent action, and the solution became milky on addition of water; ferricyanide of potassium dissolved to a yellow liquid, and nitrocyanide of titanium was unaffected.

The acid mixed with pyroxylic spirit with strong action, and with ether and alcohol. Oxalic acid, oxalate, and benzoate

of ammonium were but little affected. Paraffin was unaffected. Benzole would not mix with the acid. Spirit of turpentine exploded and produced a blood-red liquid. Gutta-percha, india-rubber, ebonite, parkesine, white wax, sealing-wax, gum-arabic, amber, copal, dammar, gamboge, juniper, kino, kowrie, shellac, and ordinary resin were rapidly disintegrated, and in nearly all cases quickly dissolved to red liquids. Spermaceti, stearic acid, and myrtle wax were but little affected. Caffeine, indigo, sugar of milk, and cane-sugar dissolved freely and rapidly. Gun-cotton dissolved instantly to a colourless liquid, which left an inflammable film on evaporation. Silk also instantly dissolved to a glutinous colourless liquid. Paper, cotton-wool, calico, gelatin, and parchment were instantly converted into glutinous substances and dissolved. Horn instantly expanded to a bulky white mass. Irish moss, German-tinder, and flannel were less rapidly affected, and sponge was less affected than any other porous organic substance. Pine-wood instantly blackened.

The chemical behaviour of such of these numerous substances with the anhydrous liquid acid as have been further examined will be more fully described in their respective places.

The *gaseous* acid carbonized cork, and acted upon wood, paper, gutta-percha, india-rubber, vulcanized india-rubber, and bees-wax more slowly, but in much the same manner as the liquid acid; sealing-wax absorbed the gas and became soft and disintegrated. It did not act upon carbon, sulphur, or selenium, nor if perfectly dry, did it act upon glass, as has been already stated (see pages 383 and 394).

From the various experiments already described, we may conclude that hydrofluoric acid is by its properties placed between hydrochloric acid and water, but is much more closely allied to the former than to the latter. It is more readily liquefied than hydrochloric acid, but less readily than steam; like hydrochloric acid it decomposes all carbonates; like water it unites powerfully with sulphuric and phosphoric anhydrides, with great evolution of heat. The fluorides of the alkali metals unite violently with anhydrous hydrofluoric acid, like the oxides of those metals unite with water; the hydrated fluorides of the alkali metals also, like the hydrated fixed alkalies, have a strongly alkaline reaction, and are capable of expelling ammonia from its salts. It may be further remarked that the atomic

number of fluorine lies between that of oxygen and chlorine; and the atomic number of oxygen, added to that of fluorine, very nearly equals that of chlorine.

B. *Aqueous Hydrofluoric Acid.*

Ordinary hydrofluoric acid is very impure; it usually contains large quantities of sulphuric acid (distilled over by excess of heat), much sulphurous acid (from action of the oil of vitriol upon the iron retort), some hydrofluosilicic acid (from silica in the spar), arsenic (from the sulphuric acid), and small amounts of hydrochloric acid, iron, lime, and other fixed matters. A sample manufactured in Birmingham, of specific gravity 1.399, was found by analysis to contain 29.58 per cent. of H_2SO_4 , and 0.5 per cent. of ignited fixed matter which had been previously precipitated by excess of ammonia; it also gave 4.08 per cent. of yellow sulphur (containing arsenic) by decomposing the sulphurous acid in it with an excess of sulphuretted hydrogen. A second sample, sent to me by the same makers, had a specific gravity of 1.310, and contained 4.8 per cent. of H_2SO_4 . A third sample, made near Birmingham, of specific gravity 1.217, contained 3.27 per cent. of H_2SO_4 and 2.16 per cent. of ignited fixed matter precipitated by ammonia, including 0.76 per cent. of silica = 1.824 per cent. of $2\text{Hf}, \text{SiF}_4$. A fourth sample, obtained from Wolverhampton, of specific gravity 1.1097, contained 0.55 per cent. of H_2SO_4 . A fifth, obtained from London, of specific gravity 1.1894, contained 10.54 per cent. of H_2SO_4 . A sixth, from Görlitz, in Prussia, of specific gravity 1.1741, contained only traces of sulphuric acid. A seventh, from Mr. Hornby, of Sheffield, of specific gravity 1.188, contained traces only of sulphuric, hydrochloric, or hydrofluosilicic acids, or of fixed matter. And an eighth sample, from Mr. William Collier, Sheffield, of specific gravity 1.248, contained no sulphuric or hydrochloric acid, and left only a trace of solid residue on evaporation to dryness: by neutralization with ammonia, 1.70 per cent. of fixed matter was obtained after washing and ignition; this fixed matter contained 1.46 part of SiO_2 = 3.5 per cent. of $2\text{Hf}, \text{SiF}_4$ in the acid; the fixed matter also contained iron, &c. A second sample, weighing twelve pounds, from the same maker gave 723 grains of sulphur by treatment with excess of sulphuretted hydrogen. All the samples contained large but

variable amounts of sulphurous acid, and gave copious deposits of sulphur, &c., by treatment with excess of sulphuretted hydrogen; they also contained very variable percentages of HF, varying from about 10 to 70. Oil of vitriol is sometimes added to weak hydrofluoric acid to enable it to etch glass in a suitable manner; it imparts to it a fictitious strength, probably by abstraction of water. A 60 per cent. acid requires dilution before it can be used for etching glass; too strong an acid etches glass roughly. An acid of 70 per cent., and containing 5.76 per cent. of H_2SO_4 , instantly converted filtering-paper into a jelly at 60°F .; it was too strong for retention in gutta-percha bottles.

Fig. 14.



A small gutta-percha jug of the annexed form was sometimes employed for taking the specific gravities of samples of weak acid. The neck of the vessel was less than half an inch internal diameter, and was closed by placing a gutta-percha ball with a handle loosely in it. Any excess of liquid above the ball was absorbed by application of sponge previous to

weighing.

Sulphurous acid is frequently present in commercial hydrofluoric acid to such an extent as to be readily detected by the odour; it may be easily found by adding shavings of metallic tin to the acid. Tin was found to be much better than zinc; it produced a cloud of sulphur at once, and evolved sulphuretted hydrogen readily. Bifluoride of tin also evolved sulphuretted hydrogen easily. Sulphuretted hydrogen gas in excess was passed through commercial hydrofluoric acid; some time after the commencement of its passage free sulphur appeared, and then accumulated quickly. No increase of sulphuric acid was found in the liquid after this reaction. If the reaction is correctly represented by the following equation, $2\text{H}_2\text{S} + \text{SO}_2 = 2\text{H}_2\text{O} + 3\text{S}$, then 95 parts by weight of sulphur separated, equal 64 parts of sulphurous acid present. One gallon of a mixture of different samples of commercial hydrofluoric acid of specific gravity 1.25 yielded by the above treatment $3\frac{1}{2}$ avoirdupois ounces of dry sulphur = 1.145 per cent. of SO_2 . Another sample yielded sulphur equal to 2.72 per cent. of SO_2 thus. I have not determined the amount of hydrochloric acid in commercial hydrofluoric acid; it is, however, quite small; nor have I ascertained the quantity of arsenic, which is also small.

The total amount of all the free acids present in a sample was roughly determined by adding a known weight of pure precipitated dry carbonate of calcium to it, until the liquid exhibited a neutral reaction to test-paper after expulsion of the liberated carbonic acid by heat. A standard solution of carbonate of sodium is inapplicable for the purpose, because the fluoride of sodium produced has an alkaline reaction.

To find the amount of free sulphuric acid, 100 grains of the acid was carefully evaporated in a platinum dish at a gentle heat until all sulphurous, hydrofluoric, hydrochloric, and hydrofluosilicic acid was expelled; the residue was then exactly neutralized by a standard solution of carbonate of sodium in the usual manner, and the amount of sulphuric acid calculated therefrom. The residuary acid liquid was in some cases diluted with water, filtered, acidified with a little hydrochloric acid, and the total amount of sulphuric acid in it determined by the ordinary gravimetric process with solution of chloride of barium.

To determine the amount of hydrofluosilicic acid, an excess of dilute aqueous ammonia was added to 100 grains of the acid previously diluted in a large platinum dish, and the silica separated from the washed precipitate (which usually contains iron and sometimes lime) in the usual manner, and weighed. 30 parts of SiO_2 equal 72 parts of HF, SiF_4 .

The most feasible method of determining the amount of HF in the impure acid consists in neutralizing it with hydrate of potash, evaporating the liquid to a small bulk, adding an excess of precipitated silica, heating the mixture with sulphuric acid, and ascertaining the amount of silica dissolved, and calculating it as fluoride of silicon (see pages 374 and 375). Numerous attempts were made to determine the amount of HF by diluting the acid, digesting it with pure precipitated silica, and calculating from the amount of silica dissolved the amount of HF present; but the results were not even approximately accurate, they were calculated too highly, apparently owing to the formation of a variable mixture of SiF_2 and HF, SiF_2 .

The sulphate-of-calcium residue from the manufacture of hydrofluoric acid is liable to contain minute amounts of potassium, sodium, lithium, thallium, and copper; also iron freely (derived from the action of the ingredients upon the iron retort), and some free sulphuric acid. Upwards of fifty-six

pounds weight of the residue was digested and washed with eight or ten gallons of distilled water, the clear liquid evaporated to small bulk in a leaden pan, and the greater portion of the free sulphuric acid expelled by heating in a platinum dish, the residue diluted, filtered, and precipitated by sulphuretted hydrogen (the yellowish-brown precipitate contained copper and thallium); most of the iron was then separated as sulphate by crystallisation, and nearly all the remainder precipitated by ammonia; the filtrate was evaporated and ignited in a platinum dish to expel the sulphate of ammonium; the ignited residue was dissolved in water and precipitated by carbonate of ammonium; the precipitate contained thallium distinctly, and the filtrate contained thallium, sodium, lithium, and potassium salts.

The following is the process employed by me for purifying ordinary hydrofluoric acid. Pass sulphuretted hydrogen through it until it contains the gas in excess; this separates the sulphurous acid (and also the arsenic if the acid is not too strong). Stir thoroughly. Find the amounts of free sulphuric and hydrofluosilicic acids present by the means already described (see page 399), and add a little more than sufficient carbonate of potassium to neutralize them, *i.e.*, 138 parts of anhydrous carbonate to 98 parts of H_2SO_4 , or 60 parts of SiO_2 .^{*} Leave it to subside until quite clear and cold, and decant the clear liquid. The effervescence, stirring, and exposure to the air expels nearly all the excess of sulphuretted hydrogen; careful addition of carbonate, oxide (or fluoride) of silver will remove the remainder. Distil the clear liquid in a leaden retort immersed in a bath of linseed-oil at a temperature varying from about 320°F. to about 460°F. , using a Liebig's condenser, containing a platinum tube to condense the vapour.† The acid requires to be redistilled once to render it quite pure. If the liquid product contains more than about 40 per cent. of anhydrous acid it will probably contain arsenic; this may be precipitated by diluting the liquid and passing a prolonged current of sulphuretted hydrogen gas through it. Avoid contact of the pure acid with

^{*} One gallon of mixed samples of ordinary hydrofluoric acid required $22\frac{1}{2}$ ounces of carbonate of potassium of 92 per cent. to neutralize its sulphuric and hydrofluosilicic acids.

† The tube employed by me was 6 feet long and $\frac{1}{2}$ inch diameter, and was kindly lent to me by Messrs. Matthey and Co.

lead vessels. (Or the following modification of the process might probably be employed:—Find amounts of sulphuric and hydrofluosilicic acids present: add more than sufficient carbonate or sulphide of potassium to neutralize them. Leave the liquid to subside, decant, and dilute it with water until it contains not more than about 40 per cent. of anhydrous acid. Pass an excess of sulphuretted hydrogen through it, filter, and distil.) I have made several gallons of the pure acid on several occasions by the first of these processes.

Hot junctions in the distillatory apparatus are best made gas-tight by vulcanized india-rubber washers, or by binding them round with ribbon of the thinnest and best quality of vulcanized rubber, secured by tarred string. Strong hydrofluoric acid containing traces of lead yielded no precipitate on addition of sulphuretted hydrogen water; nor did I succeed in removing the lead by electrolysis; it was partly precipitated by hydrochloric acid and by sulphuric acid.

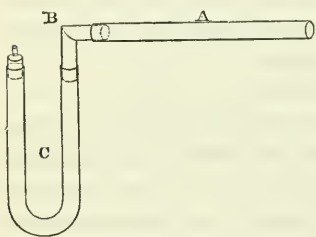
The acid prepared by the foregoing process was very pure; it yielded only a trace of fixed matter (probably derived from the gutta-percha bottle, see pages 396 and 398) on evaporation to dryness in a bright platinum dish; it evolved no sulphuretted hydrogen or sulphur by addition of zinc or tin; it gave no precipitate or colouration by addition of the following substances: excess of aqueous ammonia or of pure anhydrous carbonate of potassium, strong solution of fluoride of potassium, excess of sulphuretted hydrogen gas (either before or after neutralization of the acid by ammonia), dilute hydrochloric acid, solution of nitrate of silver, nor by adding a single drop of solution of nitrate of barium acidulated with nitric acid; it was therefore free from all impurities at all likely to be present. Additional tests were employed which need not be enumerated. This aqueous acid was employed in making the various fluorides described in this paper. I have found a plentiful supply of the pure aqueous acid of considerable service for removing (by digestion and evaporation) the silica in minerals, especially in searching for minute ingredients in those containing much silica.

The amount of anhydrous hydrofluoric acid contained in the pure aqueous acid of various degrees of strength was ascertained both by the silica-process (see pp. 374, 375, and 399) and also by the lime-process (see p. 375).

Aqueous hydrofluoric acid of a high percentage was also on

two occasions prepared by heating dry fluoride of chromium in a suitable platinum apparatus, and condensing the vapour by immersing the condensing-tube in a mixture of snow and salt. The chromium salt was prepared by precipitating a solution of chrome-alum with aqueous ammonia, and boiling with excess of the ammonia, washing the precipitate with boiling water, dissolving it whilst still wet in pure dilute hydrofluoric acid, and evaporating the solution to perfect dryness in a platinum dish. The residue was a pale green earthy powder, non-deliquescent, and very slowly soluble in water or dilute hydrofluoric acid; it lost upwards of 40 per cent. in weight of acid vapour when heated to redness in platinum vessels, without contact of the substance with the products of combustion from the gas-burner.

Fig. 15.



The following apparatus was employed:—A (fig. 15) is a retort-tube 7 inches (= 17·8 centimetres) long and $\frac{4}{8}$ of an inch (= 1·6 centim.) diameter; B is an angle-tube, and C is a curved tube about 5 inches (= 12·8 centims.) high and $\frac{1}{2}$ an inch (= 1·2 centim.) diameter. Each tube was formed of platinum without the use of solder. The

tubes fitted tightly upon each other, and the junctions were made gas-tight by means of the melted mixture of sulphur and lampblack. The outer end of the tube C was closed by a paraffin stopper containing a small platinum escape-tube.

50 grains' weight of the dry chromium salt was placed in the tube A at its closed end, and the whole tube heated somewhat above the boiling-point of water; no perceptible loss of weight occurred: the tubes were then joined together, the curved tube C immersed in snow, a wet rag laid upon A near its junction with B, and heat very *gradually* applied to the outer end of A during about twenty minutes, until about 3 inches in length of the tube was red-hot; the tube A was then taken off, the adhering cement removed, and the tube weighed; the loss of weight was 22·10 grains = 44·20 per cent. (this number, however, is a little too high because traces of the solid substance were carried forward mechanically into the angle-tube); only a trace of vapour escaped condensation. Various other fluorides besides that of chromium evolve much hydrofluoric acid when heated.

A very weak acid became concentrated to a large extent by desiccation over strong sulphuric acid in a closed leaden chamber at 60° F.; but as the concentration proceeded, the acid itself began to volatilize along with the water, until finally the vessel became empty. The sulphuric acid acquired an acid odour as if it had absorbed some of the hydrofluoric acid.

Pure aqueous hydrofluoric acid of about 40 per cent. in strength did not show any signs of solidifying by prolonged immersion in a freezing-mixture at -24° F.; nor did a mixture of two measures of that acid with one of water freeze at that temperature; but with $1\frac{1}{2}$ measure it froze imperfectly, and with 2 measures became nearly solid: no vapour of hydrofluoric acid appeared to escape during the solidification. It is evident from these experiments that a comparatively small quantity of hydrofluoric acid lowers the freezing-point of water very considerably.

The chemico-electric series of metals, &c., in pure dilute hydrofluoric acid at 60° F., containing about 10 per cent. of anhydrous acid was determined. The order obtained was as follows, the most positive substance being named first:—Aluminium, zinc, magnesium, thallium, cadmium, tin, lead, silicon, iron, nickel, cobalt, antimony, bismuth, copper, silver, gold, gas-carbon, and platinum. The aluminium evolved gas rapidly. The following series was obtained with pure hydrofluoric acid containing about 30 per cent. of anhydrous acid:—Zinc, magnesium, aluminium, thallium, indium, cadmium, tin, lead, silicon, iron, nickel, cobalt, antimony, bismuth, mercury, silver, copper, arsenic, osmium, ruthenium, gas-carbon, platinum, fused rhodium, palladium, tellurium, fused osmi-iridium, gold, iridium*. Magnesium was remarkably unacted upon by aqueous hydrofluoric acid.

The chemico-electric position of aqueous hydrofluoric acid to that of other acids was ascertained as follows:—A diaphragm of parchment-paper was fixed upon the end of a short piece of platinum tube, about $\frac{1}{2}$ an inch wide and 1 inch long, by means of a ring of gutta-percha sealed at its edge with paraffin. The acid to be compared with it was put into this porous vessel, and the vessel immersed in aqueous hydrofluoric acid contained in an outer cup of platinum. With the outer vessel connected

* I am indebted to the kindness of Messrs. Matthey and Co. for the specimens of osmium, ruthenium, rhodium, and iridium.

with one pole of a galvanometer and a sheet of platinum immersed in the inner liquid and connected with the other pole, and with acid of $28\frac{1}{2}$ per cent. in the outer vessel, the following electrical order of acids was found, the first-named being the most electro-positive:—Strong aqueous phosphoric acid, aqueous hydrofluoric acid, concentrated sulphuric acid, strong hydrochloric acid, strong nitric acid. The current in each case passed from the positive acid through the diaphragm to the other acid.

According to Faraday (Gmelin's Handbook, vol. i, p. 455) hydrated hydrofluoric acid is not decomposed by electrolysis, only the water in it is decomposed. I electrolysed dilute pure hydrofluoric acid of about 10 per cent. by means of six Smee's cells, a platinum-foil anode, and a platinum crucible cathode. Gas was liberated freely from each electrode, and a very strong odour like that of ozone was evolved. No corrosion of either electrode took place during twelve hours' action. I also electrolysed the same acid by six Grove's cells and platinum electrodes, the anode being enclosed air-tight within a gutta-percha funnel inverted in the acid, an exit-tube with a tap being in the side of the neck of the funnel for regulating the escape of the gas. Free conduction occurred. Plenty of gas was evolved. The gas from the anode smelt powerfully of ozone, and inflamed a red-hot charcoal splint vividly. Paper wet with spirits of turpentine was not blackened in the strongly issuing stream of gas, nor was bright silver affected in it. No corrosive action occurred upon the anode. I prepared some pure hydrofluoric acid containing about 80 per cent. of anhydrous acid, by taking one part by weight of 40 per cent. pure hydrofluoric acid in a bent tube C (of the apparatus, page 402) immersed in a stream of cold water, and passing through it about two parts by weight of anhydrous hydrofluoric acid vapour, obtained by very gradually fusing and heating to redness eight parts of anhydrous double fluoride of hydrogen and potassium contained in the platinum tube-retort A, to which the bent platinum tube was fixed. The acid thus obtained was electrolysed by ten Smee's cells with platinum electrodes in a narrow and deep platinum cup, the cup being the negative pole. Copious conduction occurred; a powerful odour of ozone was evolved, indicating decomposition of the water and evolution of oxygen gas at the anode; much gas was liberated, and doubtless consisted

chiefly of hydrogen. Heat was evolved in the liquid by the conduction-resistance. The anode dissolved, but not very rapidly; in three hours it lost 1.58 grain, and indicated the simultaneous decomposition of the acid with that of the water, the latter being the greatest in amount. The smell of ozone disappeared if the battery was weak, and reappeared on first contact. In a further eleven hours the anode lost 5.05 grains, and was covered with a blackish crust; this crust was partly soluble in water to a brownish solution. In a further twenty-two hours the loss had increased from 5.05 to 15.00 grains without any signs of an electro-deposit of platinum upon the platinum cathode tube. The total loss of the anode was $1.58 + 15.00$ grains = 16.58 grains. Found 15.5 grains of black-brown powder which showed some metal by pressure between surfaces of agate.

I also electrolysed pure 30 per cent. hydrofluoric acid by platinum electrodes and ten Smee's cells, the liquid being mixed with other pure acids. With equal volumes of hydrofluoric acid and concentrated nitric acid, gas was evolved freely from the anode; it had no odour of ozone, and was probably ordinary oxygen. No gas was visible at the cathode; the liberated hydrogen was doubtless absorbed by the nitric acid. Only a trace of platinum was dissolved during sixteen hours' action; the liquid was then pale yellow, but became dark green, evolved abundance of red-brown fumes, and became hot on addition of water. With equal volumes of aqueous hydrofluoric and strong hydrochloric acids, much chlorine was evolved from the anode and hydrogen from the cathode; this agrees with the usual results, that chlorides (as well as oxides) are decomposed before fluorides, and hydrochloric acid before water in electrolysis. Only a trace of chloride of platinum was formed at the anode in four hours, and the anode was not visibly corroded. With equal volumes of aqueous hydrofluoric and strong sulphuric acids much gas and a strong odour of ozone was evolved from the anode; hydrogen also from the cathode. The anode corroded very slowly, without being covered with an insoluble film, and the liquid became cloudy with suspended particles, which were light brown at first, then brown, and after many hours' action nearly black. The fumes from this mixture rapidly blackened gutta-percha. With hydrofluoric acid containing much selenious acid dissolved in it, gas was evolved from both

electrodes, and a liberal deposit of red selenium formed at the cathode. No odour of ozone occurred until a large quantity of red and black selenium (probably nearly all) was deposited upon the sides and bottom of the platinum cup, then ozone occurred strongly. The anode was not visibly corroded in twenty-eight hours' active electrolysis. The solution was filtered and evaporated to a small bulk; it then fumed densely: the odour was like that of hydrofluoric acid, and when cold the liquid was odourless and of a somewhat oily consistence. The final liquid evolved a little heat on adding water to it. I found traces of platinum in the deposited selenium. With aqueous hydrofluoric acid, to which some phosphoric anhydride had been freely added, ozone was evolved from the anode, and hydrogen from the cathode; the anode was slowly corroded, and a small quantity of black precipitate formed; the liquid remained nearly colourless.

XXXIV.—*On the Products of the Destructive Distillation of Animal Substances.*

By THOMAS ANDERSON, M.D., Professor of Chemistry in the University of Glasgow.

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IN the fourth part of these researches, I described a new base produced by the action of sodium upon picoline, to which I gave the name of Parapicoline, because it has the same composition as picoline, although the circumstances of its formation appeared to show that it had been produced by the combination of two molecules of that substance, so that its true formula would be $C_{12}H_{14}N_2$. Unfortunately, its high boiling point, and tendency to decompose when distilled, made it impossible to determine its vapour density, which afforded the only means of ascertaining whether this hypothesis was correct; and it was only assumed, because similar cases of polymerisation had been established beyond a doubt in the case of other classes of organic compounds. In the hope of obtaining a similar base of lower boiling point, and therefore better adapted to the necessary

experiments, I have submitted pyridine to the action of sodium, and the results of the inquiry are contained in the following pages.

My earlier experiments were conducted in precisely the same manner as those with picoline. Dry pyridine was heated to its boiling point along with small pieces of sodium, amounting to about one-fifth of its weight, in a flask furnished with a long cohobating tube. As the temperature rose, the pieces of sodium became covered with a brown coating; purple streaks appeared in the fluid, which, however, soon disappeared again; and after some hours the whole fluid was converted into a dark-brown or black mass, which was viscous when hot, and on cooling solidified into a hard brittle resin. In this a few white powdery nodules are disseminated, which explode violently when brought in contact with water. A large portion of the sodium employed remains unacted on, and if the operation has been well performed, is generally found collected into one or two large pieces, which can be easily separated from the resinous mass. After the sodium has been removed as thoroughly as possible, the crude product is thrown into water in small successive portions, so as to avoid the risk of explosions from any particles of sodium which may have remained disseminated through it. The water soon becomes alkaline, owing to the presence of caustic soda; unchanged pyridine makes itself manifest by its powerful smell, and the resin is slowly converted into a thick, viscid oil of dark-brown colour, and nearly, or altogether, insoluble in water, which collects at the bottom of the vessel. This oil is washed several times with water, dried over calcic chloride, and distilled. The distillation is best effected in a current of hydrogen, and at a temperature below the boiling point of the oil. A little unchanged pyridine distils at first, accompanied by a small quantity of a light oil, insoluble in water, having a pungent smell similar to, and yet appreciably different from, that of pyridine; and which, as we shall afterwards see, appears to be a mixture of several bases. As the temperature rises, a thick, heavy, and yellowish oil, having a peculiar smell, in no degree pungent, but dull, heavy, and somewhat resembling that of soot, passes over. As the distillation proceeds, crystals make their appearance in the neck of the retort. At a certain stage of the process the product becomes nearly solid, and on cooling, crystals are deposited from the

fluid distillate. Towards the close of the distillation, some ammonia and very volatile bases are evolved, obviously produced by the decomposition of the oil passing over; and a dark resinous mass remains in the retort, which can be forced over by raising the temperature, in doing which a large part of it is decomposed, and a residue of charcoal is left in the retort.

The products of the action being obviously complicated, the whole was cautiously redistilled, and the portion which solidified in the neck of the retort collected apart, while the fluid portions having been introduced into a freezing mixture of snow and salt, soon gave an abundant crop of crystals. These were purified by pressure between folds of filtering paper, and crystallisation from water or alcohol, in both of which they are soluble, until they have lost the smell of the oil by which they are accompanied.

After having proceeded some way in the investigation, I found that the same substances could be obtained with greater certainty by a modification of the process just described. It is by no means necessary to heat the sodium and pyridine together, for the action takes place in the cold; but in this case it is slower, and the phenomena are somewhat different. The brown appearance on the surface of the sodium and the purple streaks appear in the fluid at the beginning of the action, but the pyridine does not become brown, it retains its colour, and the sodium is covered with a black crust, which, after two or three days, exceeds it in bulk, is quite brittle, and sometimes shows a tendency to separate into layers. The pyridine acquires a yellowish tint, and then contains in solution an oil insoluble in water. When the action is judged to have gone sufficiently far, the sodium with its crust is removed from the fluid and washed with a small quantity of pure pyridine, so as to get rid of any of the oily base which may remain attached to it. The crust is then detached as thoroughly as possible from the sodium and thrown into water, any sodium still adhering to it burns, and a dark grey, almost black, powder falls to the bottom of the glass. This is washed, first by decantation, and afterwards on a cloth filter until it is free from soda, and on being opened out and exposed for some time to the air, it is entirely converted into a snow-white mass of interlaced acicular crystals identical with those obtained by the first process.

DIPYRIDINE.

The substance so obtained is a base to which, for reasons that will be immediately apparent, I give the name of dipyridine. It forms white crystals fusing at 108° C., and solidifies on cooling into a crystalline mass. It volatilizes slowly at 100° , and sublimes unchanged at a high temperature, giving long needle-shaped crystals. It is rather sparingly soluble in cold but readily in boiling water, and the fluid, on cooling, becomes filled with a mass of interlaced needles. It is readily soluble in alcohol and ether, and the boiling solutions give acicular crystals on cooling. It likewise dissolves in pyridine and in volatile oils. From the oily base along with which it distils in the first process of preparation, it crystallises in short, thick, four-sided prisms, which are transparent so long as they remain in the fluid, but soon become opaque when they are removed from it. When well purified they are inodorous, but in general they have a faint smell, due, apparently, to a trace of the fluid base adhering to them. Dipyridine is a very stable compound. It is not decomposed by hydrochloric, sulphuric, or nitric acid. Potash and ammonia precipitate it from its solutions in acids as a mass of minute crystals. Its aqueous solution gives no precipitates with solutions of sulphate of magnesia, zinc, nickel, acetate of lead, or perchloride of iron. With sulphate of copper it gives a pale bluish-white precipitate; with corrosive sublimate a white amorphous powder insoluble in boiling water; and with nitrate of silver a white precipitate insoluble in cold and sparingly in boiling water, from which the compound is obtained in crystals on cooling. Its most characteristic reactions, however, are those it gives with the ferro- and ferri-cyanides of potassium. If a few drops of the ferro-cyanide of potassium be added to a not too dilute solution of the dipyridine hydrochlorate, a pale precipitate makes its appearance, which rapidly changes to a dirty indigo colour, increasing at the same time in quantity. If the proper concentration is hit, the precipitate consists entirely of very minute needle-shaped crystals having a dark indigo colour. They dissolve in boiling water, forming a very deep and rather dull purple solution, and are again deposited on cooling; but if the boiling be continued for some time, the compound appears to undergo some change, for the

fluid retains its red colour at ordinary temperatures, though a great part of the substance is still deposited in crystals. A saturated cold solution of dipyridine in water gives no precipitate with ferrocyanide of potassium; but on the addition to the mixture of a drop or two of hydrochloric acid, the dark precipitate instantly makes its appearance, and is deposited in small crystals. The precipitate is readily soluble in excess of hydrochloric acid. When ferriecyanide of potassium is added to dipyridine hydrochlorate, no immediate effect is observed, but on standing, the interior of the test-tube becomes lined with minute prisms of sulphur-yellow colour and high lustre. If the solution be boiled, it acquires a dark colour, and partial decomposition takes place.

Dipyridine carefully dried in the water-bath was found on analysis to give these results:—

	Experiment.		Calculation.		
	I.	II.			
Carbon	75.74	76.07	75.94	C ₅	60
Hydrogen..	5.94	5.83	6.33	H ₅	5
Nitrogen ..	—	—	17.73	N	14
			100.00		79

These numbers lead to the formula C₅H₅N, which is that of pyridine itself.

The platinum compound of the base, which is thrown down as a yellow crystalline powder, gave the following results:—

	Experiment.			Calculation.		
	I.	II.	III.			
Carbon	—	—	20.78	21.02	C ₁₀	120
Hydrogen..	—	—	2.48	2.10	H ₁₂	12
Nitrogen ..	—	—	—	4.90	N ₂	28
Chlorine ..	—	—	—	37.30	Cl ₆	213
Platinum ..	34.11	34.12	34.03	34.68	Pt	197.4
				100.00		570.4

This agrees with the formula (C₅H₅NHCl)₂PtCl₄, which is identical with that of the pyridine salt. In order to fix the true

constitution of the base, it was necessary to determine its vapour-density, and as its boiling point was beyond the range of the mercurial thermometer, it was necessary to use a bath of metallic lead and an air thermometer. The air thermometer was a bulb of the same size as that used for containing the vapour. The density of the vapour found by experiment was 5.92. The formula $C_{10}H_{10}N_2$ requires 5.46. This result is as close as could be expected under the circumstances, and proves that the base must be formed by the combination of two molecules of pyridine, and hence the name of dipyridine, which I have applied to it.

Salts of Dipyridine.—Though dipyridine is not a very powerful base, it gives a number of salts, most of which crystallise well, though some of them are not easily obtained of definite composition.

Hydrochlorate of Dipyridine ($C_{10}H_{10}N_2 \cdot 2HCl$).—This salt is best obtained by adding a slight excess of hydrochloric acid to the aqueous solution of the base and evaporating to crystallisation; the crystals, after being pressed and recrystallised from water, are sufficiently pure for analysis. They are flat needles readily soluble in water, especially when hot—insoluble in ether. The salt is very apt to retain hydrochloric acid, and it is advisable to heat it to 130° for analysis.

Sulphate of Dipyridine.—Dipyridine is added in slight excess to dilute sulphuric acid, and this fluid is evaporated nearly to dryness; on cooling, crystals of the sulphate are deposited; they are washed with alcohol, in which they are scarcely soluble, and again crystallised from water. It is thus obtained in needle-shaped crystals, which deliquesce in moist air. One determination of sulphuric acid was made of a specimen of this salt dried in vacuo over sulphuric acid, which gave 26.85 per cent. of SO_3 . This would correspond with a salt containing two molecules of water of crystallisation with the formula $C_{10}H_{10}N_2 \cdot H_2SO_4 + 2H_2O$, which requires 27.39 per cent.

Nitrate of Dipyridine ($C_{10}H_{10}N_2 \cdot 2HNO_3$) is obtained by adding a slight excess of nitric acid to solution of dipyridine, evaporating on the water-bath and recrystallising. It forms pale yellow needles of moderate solubility in water. When exposed for some time to a temperature of 100° , it acquires an orange colour, but is not sensibly decomposed.

Double Salt with Chloride of Zinc ($C_{10}H_{10}N_2 \cdot 2HCl \cdot ZnCl_2$).—

This substance is prepared by adding to dipyrindine a mixture of hydrochloric acid and zinc chloride, and allowing it to stand for some time, when small prismatic crystals are deposited. Their formation is materially assisted by the addition of alcohol and ether. The compound may even be obtained from the crude product, in which the dipyrindine is mixed with the oily base distilling along with it. For this purpose zinc chloride, along with hydrochloric acid and a considerable excess of alcohol and ether, must be added to the crude product, when, especially on stirring, the zinc salt deposits, and can be purified by crystallisation from water. This process can even be employed for separating the two bases. The salt is in long white needles, soluble in eight times their weight of water, less so in alcohol, and quite insoluble in ether. On the addition of potassic hydrate in excess it gives the pure base in minute crystals.

Double Salt with Nitrate of Silver.—This salt is best obtained by mixing hot solutions of dipyrindine hydrochlorate and silver nitrate, the latter being in excess, and at once filtering off the precipitated silver chloride. On cooling, the salt is deposited in brilliant needles, of sparing solubility in water. This compound could not be obtained of constant composition, but one specimen gave 35.09 per cent. of silver, while the formula $C_{10}H_{10}N_2(HNO_3)_2(AgNO_3)_2$ requires 34.61.

Platino-chloride of Dipyrindine.—The analysis of this salt has been already given. It is obtained as a crystalline yellow powder of very sparing solubility.

Palladio-chloride of Dipyrindine is obtained as an orange precipitate on mixing the hydrochlorates.

DERIVATIVES OF DIPYRIDINE.

Diethylo-Dipyrindine.—The compounds of this base were obtained in the usual manner. The ethyl-iodide, $C_{10}H_{10}N_2(C_2H_5I)_2$, is easily prepared by exposing dry dipyrindine with iodide of ethyl to the temperature of 100° in hermetically-sealed tubes. The action is complete in half an hour. It is obtained in acicular crystals, which are brilliant and perfectly colourless if they have not been exposed to the air. They are very soluble in water, much less so in alcohol and in ether.

Heated with silver chloride and water this salt was converted into the chloride, which, on the addition of platinic-chloride

gave the platino-chloride in very sparingly soluble small red needles, having the composition $C_{10}H_{10}N_2(C_2H_5Cl)_2PtCl_4$.

The base itself, when separated from the iodide by silver oxide, forms a highly alkaline solution, having generally a red or purple colour, which, on evaporation, leaves a dark-coloured uncrystallised residue. It obviously belongs to the class of ammonium bases, but I have not pursued its investigation further.

Dibromo-Dipyridine ($C_{10}H_8Br_2N_2$).—This base is thrown down when bromine is added to a solution of dipyridine hydrochlorate, or hydrobromate, as a white powder, insoluble in water, sparingly soluble in cold, more so in hot alcohol, from which it is deposited in flattened needles on cooling. If too much bromine has been used in its preparation, these crystals are pink. Its basic properties are extremely feeble, and it is a somewhat unstable compound; for, on boiling with water, or with hydrochloric acid, the original base appears to be more or less completely regenerated.

Its platinum compound could not be obtained in a state fitted for analysis. On boiling with hydrochloric acid, and adding platinic chloride, a yellow precipitate was obtained, which, in one experiment, gave 32.39 per cent. of platinum; and in another, in which the boiling was continued longer, 33.53 per cent. was obtained. Dibromo-dipyridine requires 30.94, and dipyridine itself 34.68; so that there can be little doubt that the latter has been regenerated.

OILY BASE.

The oily base from which the dipyridine was deposited in crystals, has been as yet but imperfectly examined. It was purified by redistillation and cooling, by which it yielded a small additional quantity of dipyridine, and this was repeated as long as it gave crystals. The base so obtained is a rather thick, pale-yellow oil, heavier than water, having a peculiar heavy smell, quite distinct from that of pyridine. It is insoluble in water, but dissolves with great ease in alcohol and ether. It boils at a high temperature, and if distilled rapidly, undergoes partial decomposition, yielding a small quantity of what appears to be a mixture of several bases with pungent smell, and sparingly soluble in water. If, however, the distillation be

carried on very cautiously at a temperature below its boiling point, it passes over unchanged. It dissolves in acids and forms salts, most of which, however, are uncrystallisable, and dry up into gummy masses. It was prepared for analysis by drying over calcic chloride, distilling and separating the first part of the distillate which might retain moisture.

	Experiment.		Calculation.		
	I.	II.			
Carbon	76.59	75.51	75.94	C ₅	60
Hydrogen. .	6.94	6.98	6.33	H ₅	5
Nitrogen ..	—	—	17.73	N	14
			<hr/> 100.00		<hr/> 79

These results, it will be seen, correspond with those given by pyridine and dipyridine, and they are confirmed by the analysis of a platinum salt, prepared in the usual way, which gave 33.94 per cent. platinum, and calculation for the formula $(C_5H_5NHCl)_2PtCl_4$ requires 34.68. It is obvious, therefore, that this is another polymer of the original pyridine; but, unfortunately, there is no means by which its molecular constitution can be determined. It is impossible to determine its vapour density, because it undergoes partial decomposition at its boiling point; and as its salts do not crystallise, and probably, like the platinum compound, all correspond with those of the original pyridine, there is no prospect of satisfactory conclusions being drawn from them. In the absence of experimental evidence, any assumption may be made regarding the constitution of this base, and at first sight the most reasonable view of the matter is to suppose it to be the product of a further polymerisation, and to be formed by the combination of three or four molecules of the original pyridine. Its boiling point, which is certainly lower than that of dipyridine, however, appears to militate against this view; and taking its properties and those of its compounds into consideration, I am inclined to believe it to be another dipyridine, and an example of those cases of physical isomerism of which so many are now known. As there was no means of ascertaining the constitution of this base, and the properties of its compounds were not encouraging, I have not pursued their investigation further.

LIGHT BASES.

It has been stated at the commencement of this paper that when dipyridine was prepared by the first of the processes there described, a light basic oil was obtained at the beginning of the rectification of the crude product. This oil, which is insoluble in water, was collected, dried, and rectified, when it was found to consist of several bases. The distillate was collected in several fractions, which were analysed, but the quantity was far too small to admit of any systematic attempt to separate them. The results, both of the combustion of the bases themselves and of the platinum determinations in their platinum compounds, seem to show that they are a class of bases isologous with the pyridine series. I give here the results of these analyses:—No. I, boiled between 225° and 240° F.; II, between 270° and 290° F.; III, about 291° F.; IV, between 287° and 291° F.; V, between 291° and 360° F.

	I.	II.	III.	IV.	V.
Carbon	75·51	75·36	76·18	74·23	77·47
Hydrogen . .	8·46	8·71	8·13	8·58	8·47
Nitrogen ..	16·03	15·93	15·69	17·19	14·06
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

It must be distinctly understood that all the substances analysed were obviously mixtures, and the degrees above given do not denote true boiling points, but only that the fractions they represent were collected at these points. It will be observed that all these analyses are characterised by yielding a percentage of hydrogen far above that contained in pyridine, or any of its homologues. To render this more obvious, I place here the calculated numbers for pyridine and picoline, along with those required by bases containing two atoms of hydrogen more than these compounds:—

	C_5H_5N .	C_6H_7N .	C_5H_7N .	C_6H_9N .
Carbon	75·94	77·42	74·04	75·75
Hydrogen ..	6·33	7·53	8·64	9·47
Nitrogen ..	17·73	15·05	17·32	14·78
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

The experimental results above given are manifestly incompatible with the first two of these formulæ, but would agree tolerably with a mixture of substances containing more hydrogen, and this is further confirmed by several platinum determinations in platinum compounds obtained from these substances. These results appear to indicate the existence of a series of bases having the general formula $C_nH_{2n-3}N$. The further investigation of these substances would be of interest, but as they are obtained only in minute quantity, and are clearly secondary products of the action of sodium on pyridine, it is scarcely possible to obtain them in sufficient quantity for this purpose.

At the beginning of this paper, mention has been made of a black or dark-grey substance, obtained in the second process for preparing dipyrindine. This compound was only obtained towards the close of the investigation, and I have not had time to examine its properties and relations minutely. It is a black amorphous powder, quite insoluble in water. When exposed to the air, it is rapidly converted into a mass of crystals of pure dipyrindine. I was at first disposed to consider this substance to be a sodium-compound of dipyrindine, but I soon found that this was not the case, and that its properties more nearly corresponded with a hydrogen-compound of that base; and it seems probable that its formula will turn out to be $C_{10}H_{12}N_2$, in which case it would be related to dipyrindine in the same manner as ammonium is to ammonia. Should this view be correct, it seems probable that, on the addition of hydrochloric acid, it should, like a metal, evolve hydrogen. An experiment was made to ascertain whether this occurred, by introducing a quantity of the compound into a jar over mercury, and bringing hydrochloric acid in contact with it; but the anticipated result was not obtained,—no hydrogen was evolved, but a brownish precipitate appeared in the fluid, and the grey powder at once disappeared. I have been unable to pursue this subject further, but propose to return to it on a future occasion.

Numerous experiments have been made, in the hope of throwing light on the nature of the chemical changes occurring during the first process of preparing dipyrindine; but they are obviously of a very complex kind, and some of the products must be the result of secondary decompositions. My impression is, that sodio-dipyrindine must be first formed, probably $C_{10}H_8Na_2N_2$.

In this case hydrogen must be given off during the action, and this is actually the case, as was established by direct experiment; but the quantity evolved is trifling compared with that of the sodium consumed, so that if the action takes place in this way, a large part of the hydrogen must be converted into some other compounds within the mixture itself. The light bases already mentioned might account for this, if it were not that they are produced in very small quantity. Altogether I am inclined to think that, in the first process, a number of secondary reactions take place, which greatly complicate matters, and that it is through some modification of the second by which an explanation will most probably be obtained. I am still engaged with the subject, and have already nearly perfected a process by which some of the products can be obtained with greater certainty and in larger quantity than by either of those described in this paper, and which I hope will enable me to subject the constitution and relations of these curious compounds to a more minute examination.

XXXV.—*On the Products of the Action of Nitric Acid on the Resinous Extract of Indian Hemp.*

By THOMAS BOLAS, F.C.S., and ERNESTE E. H. FRANCIS,
Demonstrator in Chemistry, Charing Cross Hospital.

FOUR ounces of the commercial resinous extract of Indian hemp (*Cannabis indica*) were treated with 30 oz. of nitric acid, sp. gr. 1.32; a violent action accompanied by a copious evolution of nitrous fumes took place. When the action had in a great measure subsided, the flask was heated for five hours in a water-bath; it was then taken out and allowed to cool; when cold, the acid liquor was decanted from a resinous substance, and evaporated to dryness on the water-bath. The resinous substance which remained in the flask was treated with 20 oz. of nitric acid, sp. gr. 1.42, and boiled for eight hours in a long-necked flask. After having stood all night, the clear acid liquor was poured into the basin containing the residue from the first

evaporation; it was then evaporated to dryness on the water-bath. A resinous portion remaining in the flask was again treated with nitric acid, and so on until the whole of the resinous substance was dissolved.

The substance obtained by the evaporation of the acid liquors was dissolved in warm nitric acid, sp. gr. 1.42, evaporated a little, and allowed to cool. The substance which was deposited was washed with cold water, and dissolved in hot methylated spirit, from which it crystallised in long flat prisms. It was purified by two recrystallisations from spirit.

The substance thus obtained does not appear to be an acid, as it is not apparently changed by being boiled with moderately strong potash, soda, or ammonia, and its alcoholic solution is neutral to test-paper. It does not contain nitrogen. When pure it is white, with a slight tinge of yellow. When heated on platinum foil it melts and burns, leaving a slight carbonaceous residue, which disappears on the further application of heat. Heated in a tube, it melts at $175\text{--}176^{\circ}\text{C}$., and on the further application of heat it sublimes without leaving a residue, while a sublimate, consisting of long asbestos-like needles, condenses on the upper part of the tube. It is insoluble in water and tasteless, slightly soluble in alcohol, from which it crystallises in long flat prisms. In hot nitric acid it dissolves, and on evaporation separates unchanged. It is soluble in oil of vitriol, the solution becoming blackened on the application of heat. It is soluble in benzol and chloroform, insoluble in bisulphide of carbon and ether. This substance, which we propose at present to call oxy-cannabin, is probably formed by the oxidation of some principle contained in the extract. It gave on combustion numbers agreeing with the formula $\text{C}_5\text{H}_6\text{O}_2$.

I. .2329 grm. gave .5210 grm. CO_2 and .1324 grm. H_2O .

II. .3850 grm. gave .8610 grm. CO_2 , and .2148 grm. H_2O .

		Theory.	I.	II.	Mean.
C_5	= 60	61.23	61.01	60.99	61.00
H_6	= 6	6.12	6.31	6.20	6.25
O_2	= 32	32.65			
	—	—			
	98	100.00			

The acid liquors which have deposited oxy-cannabin yield,

on further evaporation, a small quantity of an acid substance which crystallises in plates, but which we did not obtain in a state of purity.

XXXVI.—*On the Relation of Hydrogen to Palladium.*

By the late THOMAS GRAHAM, F.R.S.

[Abstracted from the Proceedings of the Royal Society, vol. xvii, pp. 212, 500.]

It has often been maintained on chemical grounds that hydrogen gas is the vapour of a highly volatile metal. The idea forces itself upon the mind that palladium with its occluded hydrogen is simply an alloy of this volatile metal in which the volatility of the one element is restrained by its union with the other, and which owes its metallic aspect equally to both constituents. How far such a view is borne out by the properties of the compound substance in question will appear by the following examination of the properties of what, assuming its metallic character, would fairly be named *hydrogenium*.

Density.—The density of palladium when charged with 800 or 900 times its volume of hydrogen gas is perceptibly lowered; but the change cannot be measured accurately by the ordinary method of immersion in water, owing to a continuous evolution of minute hydrogen bubbles, which appears to be determined by contact with the liquid. However, the linear dimensions of the charged palladium are altered so considerably that the difference admits of easy measurement, and furnishes the required density by calculation. Palladium in the form of wire is readily charged with hydrogen by evolving that gas upon the surface of the metal in a galvanometer containing dilute sulphuric acid, as usual.* The length of the wire before and after a charge is found by stretching it on both occasions with the same moderate weight, such as will not produce permanent distention, over the surface of a flat graduated measure. The measure used was graduated to hundredths of an inch, and by means of a vernier, the divisions could be read to thousandths. The distance be-

* Proceedings of the Royal Society, xvi, 422.

tween two fine cross lines marked upon the surface of the wire near each of its extremities was observed.

A hard and elastic wire was drawn from welded palladium; its diameter was 0.462 millimetre, and its specific gravity 12.38, as determined with care. The wire was twisted into a loop at each end, and a mark was made near each loop. The loops were varnished so as to limit absorption of gas by the wire to the measured length between the two marks. To straighten the wire, one loop was fixed, and the other connected with a string passing over a pulley and loaded with 1.5 kilogramme, a weight sufficient to straighten the wire without occasioning any undue strain. The wire was charged with hydrogen by making it the negative electrode of a small Bunsen's battery consisting of two cells, each of half a litre in capacity. The positive electrode was a thick platinum wire placed side by side with the palladium wire, and extending the whole length of the latter, within a tall jar filled with dilute sulphuric acid. The palladium wire had, in consequence, hydrogen carried to its surface for a period of one and a half hour. A longer exposure was found not to add sensibly to the charge of hydrogen acquired by the wire. It was again measured and the increase in length noted. Finally, after being dried with a cloth, it was divided at the marks, and the charged portion heated in a long narrow glass tube kept vacuum by a Sprengel aspirator. The whole occluded hydrogen was thus collected and measured, its volume being reduced by calculation to Bar. 760 mm., and Therm. 0° C.

The original length of the palladium wire exposed was 609.144 mm. (23.982 inches), and its weight 1.6832 gm. The wire received a charge of hydrogen amounting to 936 times its volume, measuring 128 c.c., and therefore weighing 0.01147 gm. When the gas was ultimately expelled, the loss, as ascertained by direct weighing was 0.01164 gm. The charged wire measured 618.923 mm., showing an increase in length of 9.779 mm. (0.385 inch). The increase in linear dimensions was from 100 to 101.605; and in cubic capacity, assuming the expansion to be equal in all directions, from 100 to 104.908. Supposing the two metals united without any change of volume, alloy may therefore be said to be composed of—

	By volume.	
Palladium	100	or 95.32
Hydrogenium.....	4.908	or 4.68
	<hr/> 104.908	<hr/> 100

The expansion which the palladium undergoes appears enormous if viewed as a change of bulk in the metal only, due to any conceivable physical force, amounting as it does to sixteen times the dilatation of palladium when heated from 0° to 100° C. The density of the charged wire is reduced by calculation from 12.3 to 11.79. Again, as 100 is to 4.91, so the volume of the palladium, 0.1358 c.c. is to the volume of the hydrogenium 0.006714 c.c. Finally, dividing the weight of the hydrogenium, 0.01147 grm. by its volume in the alloy, 0.006714 c.c., we find

Density of hydrogenium..... 1.708

Six other closely agreeing experiments, made in a similar manner, gave, as the mean density of hydrogenium, the number 1.951, or nearly 2. But this result is subject to an important correction, as will be seen hereafter (p. 424).

The expulsion of hydrogen from the wire, however caused, is attended with an extraordinary contraction of the latter. On expelling the hydrogen by a moderate heat, the wire not only receded to its original length, but fell as much below that zero as it had previously risen above it. The palladium wire, which first measured 609.144 mm., and increased 9.77 mm., was ultimately reduced to 599.444 mm., and contracted 9.7 mm. The wire was permanently shortened. The density of the palladium did not increase, but fell slightly at the same time, namely from 12.38 to 12.12; proving that this contraction of the wire is in length only. The result is the converse of extension by wire-drawing. The retraction of the wire is possibly due to an effect of wire-drawing in leaving the particles of metal in a state of unequal tension, a tension which is excessive in the direction of the length of the wire. The metallic particles would seem to become mobile, and to right themselves in proportion as the hydrogen escapes; and the wire contracts in length, expanding, as appears by its final density, in other directions at the same time.

A wire so charged with hydrogen, if rubbed with the powder

of magnesia (to make the flame luminous), burns like a wax thread when ignited in the flame of a lamp.

It is necessary to assume, in this discussion, that the two metals do not contract nor expand, but remain of their proper volume on uniting. Dr. Matthiessen has shown that in the formation of alloys generally the metals retain approximately their original densities.*

On charging and discharging portions of the same palladium wire repeatedly, the curious retraction was found to continue, and seemed to be interminable. The following expansions, caused by variable charges of hydrogen, were followed on expelling the hydrogen by the retractions mentioned :—

	Elongation.	Retraction.
1st experiment	9.77 mm.	9.70 mm.
2nd „ 	5.765 „	6.20 „
3rd „ 	2.36 „	3.14 „
4th „ 	3.482 „	4.95 „
		<hr/> 23.99

The palladium wire, which originally measured 609.144 mm., has suffered by four successive discharges of hydrogen from it, a permanent contraction of 23.99 mm. ; that is, a reduction of 5.9 per cent. in its original length. The contractions will be observed to exceed in amount the preceding elongations produced by the hydrogen, particularly when the charge of the latter is less considerable. With another portion of wire the contraction was carried to 15 per cent. of its length by the effect of repeated discharges. The specific gravity of the contracted wire was 12.12, no general condensation of the metal having taken place. The wire shrinks in length only.

In the preceding experiments the hydrogen was expelled by exposing the palladium, placed within a glass tube, to a moderate heat short of redness, and exhausting by means of a Sprengel tube; but the gas was also withdrawn in another way, viz., by making the wire the positive electrode, and thereby evolving oxygen upon its surface. In such circumstances, a slight film of oxide of palladium is formed on the wire, but it appears not to interfere with the extraction and oxidation of the hydrogen. The wire measured—

* Philosophical Transactions, 1860, p. 177.

		Difference.
Before charge	443.25 mm.	
With hydrogen.	449.90 „	+ 6.65 mm.
After discharge.	437.31 „	— 5.94 „

The retraction of the wire, therefore, does not require the concurrence of a high temperature. This experiment further proved that a large charge of hydrogen may be removed in a complete manner by exposure to the positive pole—for four hours in this case; for the wire in its ultimate state gave no hydrogen on being heated *in vacuo*.

The wire, which had been repeatedly charged with hydrogen, was once more exposed to a maximum charge, for the purpose of ascertaining whether or not its elongation under hydrogen might now be facilitated and become greater, in consequence of the previous large retraction. No such extra elongation, however, was observed on charging the retracted wire more than once; and the expansion continued to be in the usual proportion to the hydrogen absorbed. The final density of the wire was 12.18.

The wire retracted by heat is found to be altered in another way, which appears to indicate a molecular change. When the gas has been expelled by heat, the metal gradually loses much of its power to take up hydrogen. The last wire, after it had already been operated upon six times, was again charged with hydrogen for two hours, and was found to occlude only 320 volumes of gas, and in a repetition of the experiment, 330.5 volumes. The absorbent power of the palladium had therefore been reduced to about one-third of its maximum.

The condition of the retracted wire appeared, however, to be improved by raising its temperature to full redness, by means of an electrical current from a battery. The absorption rose thereafter to 425 volumes of hydrogen, and in a second experiment to 422.5 volumes.

The wire becomes fissured longitudinally, acquires a thready structure, and is much disintegrated on repeatedly losing hydrogen, particularly when the latter has been extracted by electrolysis in an acid fluid. The palladium in the last case is dissolved by the acid to some extent. The metal appeared, however, to recover its full power to absorb hydrogen; it now condensed upwards of 900 volumes of gas.

The effect upon its length of simply annealing the palladium wire by exposure in a porcelain tube to a full red heat, was observed. The wire measured 556.075 mm. before, and 555.875 mm. after heating; or a minute retraction of 0.2 mm. was indicated. In a second annealing experiment, with an equal length of new wire, no sensible change of length could be discovered. There is no reason, then, to ascribe the retraction, after absorption of hydrogen, in any degree to the heat applied when the gas is expelled. Palladium wire is very slightly affected in physical properties by such annealing, retaining much of its first hardness and elasticity.

The permanent shortening of the palladium wire, observed after the expulsion of the hydrogen, leads to an important correction in the density of hydrogenium, as above calculated. In the experiment above described (p. 420), the elongation was 9.78 mm., and the absolute shortening in retraction 9.7 mm., making the absolute difference of length 19.48 mm. The elongation and retraction would appear, indeed, to be equal in amount. Now, it is by no means impossible that the volume added to the wire is represented by the elongation and retraction together, and not by the elongation alone, as hitherto assumed. It is only necessary to suppose that the retraction of the palladium-molecules takes place at the moment when the hydrogen is first absorbed, instead of being deferred till the latter is expelled; for the righting of the particles of the palladium wire (which are in a state of excessive tension in the direction of its length) may as well take place in the act of absorption of the hydrogen, as in the act of expulsion of that element. It may, indeed, appear most probable in the abstract that the mobility of the palladium particle is determined by the first entrance of the hydrogen. The hydrogenium will then be assumed to occupy double the space previously allotted to it, and its density will be reduced to one-half of the former estimate. In the experiment referred to, the volume of hydrogenium in the alloy will rise from 4.38 to 9.36 per cent., and the density of the hydrogenium will fall, according to the new calculation, from 1.708 to 0.854. In a series of four observations on the same wire, above recorded, the whole retractions rather exceeded the whole elongations, the first amounting to 23.99 mm., and the last to 21.38 mm. Their united amount would justify a still fur

ther reduction in the density of hydrogenium, namely, to 0·8051.

The first experiment, however, in hydrogenising the palladium wire appears to be the most uniform in its results. The subsequent expulsion of the hydrogen by heat always injures the structure of the wire more or less, and probably affects the regularity of the expansion afterwards in different directions. The equality of the expansion and retraction in a first experiment appears also to be a matter of certainty. This is a curious molecular fact, the full import of which cannot as yet be seen. In illustration, another experiment upon a pure palladium wire may be detailed. This wire, which was new, took up a full charge of hydrogen, viz., 956·3 volumes, and increased in length from 609·585 to 619·334 mm. The elongation was, therefore, 9·769 mm. With the subsequent expulsion of the hydrogen, the wire was permanently shortened to 600·115 mm. It thus fell 9·470 mm. below its normal or first length. The elongation and retraction are here within 0·3 mm. of equality. The two charges together amount to 19·239 mm., and their sum represents the increase of the wire in length, due to the addition of hydrogenium. It represents a linear expansion of 3·205 on 100, with a cubic expansion of 9·827 on 100. The composition of the wire comes, then, to be represented as being—

Palladium	100·000 or 90·825
Hydrogenium	9·827 „ 9·105
	<hr/>
	109·827 100·000

The specific gravity of the palladium was 12·3, the weight of the wire was 1·554 gm., and its volume 0·126 cub. centim. ($100 : 9·827 = 0·126 : 0·01238$). The density of the hydrogenium is therefore

$$\frac{0·0108}{0·01238} = 0·872.$$

This is a near approach to the preceding result, 0·854. Calculated on the first method, the last experiment would give a density of 1·744.

Palladium alloys, as well as palladium itself, have the power of occluding hydrogen, when the second metal does not much exceed one-half of the mixture. These alloys are all enlarged

in dimensions when they acquire hydrogenium. The expansion is greater than that which occurs in pure palladium (about twice as much), and on afterwards expelling the hydrogen by heat, the fixed alloy returns to its original length, *without any further shortening of the wire*. The embarrassing retraction of the palladium has, in fact, disappeared.

The alloys were fused in a Deville's gas-furnace when the proportion of palladium was considerable, or in a coke furnace when the materials yielded to a milder temperature. The alloy was always, if possible, drawn out into thin wire, but if not sufficiently ductile, it was rolled into a thin ribbon. The elongation was measured, as before, by stretching the wire or ribbon over a graduated scale.

An alloy of palladium and platinum, containing 23·97 parts of the latter metal, very malleable and ductile, of sp. gr. 12·64, rapidly absorbed hydrogen evolved on its surface in the acid liquid of the galvanic cells. A wire of this alloy, 601·845 mm. (23·69 inches) long, upon occluding 701·9 vol. hydrogen gas, measured at 0° C., and 0·76 bar, was increased to 618·288 mm. This is a linear elongation of 16·443 mm. (0·6472 inch), or 2·732 on a length of 100. It corresponds with a cubic expansion of 8·423 volumes on 100 volumes, and the product may be represented as follows:—

	In volume.	
Fixed metals	100·000	or 92·225
Hydrogenium	8·423	„ 7·775
	<hr/> 108·423	<hr/> 100·000

The elements for the calculation of the density of hydrogenium are the following, the assumption being made, as formerly, that the elements are united without condensation:—

Original weight of the wire, 4·722 grms.

Original volume of the wire, 0·373 cub. centim.

Volume of the hydrogen extracted, 264·5 cub. centim.

Weight (by calculation) of the hydrogen extracted, 0·0237 gm.

The volume of the hydrogenium will be to the volume of the wire (0·0237 cub. centim.) as 100 : 8·423, that is, 0·3141 cub. centim. Finally, dividing the weight of the hydrogenium

by its bulk, 0·0237 by 0·3141, the density of the hydrogenium is found to be 0·7545.

On expelling the hydrogen from the wire at a red heat, the latter returned to its first dimensions as exactly as could be measured. The platinum present appears to sustain the palladium, so that no retraction is allowed to take place. This alloy, therefore, displays the true increase of volume following the acquisition of hydrogenium, without the singular complication of the retraction of the fixed metal. It now appears clear that the retraction of pure palladium must occur on the first entrance of hydrogen into the metal. The elongation of the wire, due to the hydrogenium, is thereby negatived to the extent of about one-half, and the apparent bulk of the hydrogenium is reduced to the same extent.

The compound alloy returns to its original density (12·64) on the expulsion of the hydrogen, showing that the latter escapes without producing porosity in the metal. No absorptive power for vapours, like that of charcoal, was acquired.

A wire of the alloy above described, and another of pure palladium, were both charged with hydrogen, and the diameters of both were measured by a micrometer. The wire of alloy increased sensibly less in thickness than the pure palladium only about half an inch; the reason is, that the latter, while expanding, retracts in length at the same time. The expansion of the two wires may be familiarly compared to the enlargement of the body of a leech while absorbing blood. The enlargement is uniform in all dimensions with the palladium-platinum alloy; the leech becomes larger, but remains symmetrical. But the retraction of the pure palladium wire has its analogy in a muscular contraction of the leech, by which its body becomes shorter, but thicker in a corresponding measure.

The same wire of palladium and platinum, charged a second time with hydrogen, underwent an increase in length from 601·845 to 618·2, or sensibly the same as before. The gas measured 258·0 cub. centim., or 619·6 times the volume of the wire. The product may be represented as consisting of

	By volume.
Fixed metals	92·272
Hydrogenium.....	7·728
	<hr/>
	100·000

The density of hydrogenium deduced from this experiment is 0·7401; the mean of the two experiments is 0·7473.

Similar experiments were made with alloys of palladium with *gold* and with *silver*. The results, together with the preceding, are given in the following table:—

	Observed density of hydrogenium.
When united with palladium.... .	0·854 to 0·872
When united with palladium and platinum	0·7401 to 0·7545
When united with palladium and gold	0·711 to 0·715
When united with palladium and silver	0·727 to 0·742

These results are most uniform with the compound alloys, in which retraction is avoided, and they lie between 0·711 and 0·7545. It may be argued that hydrogenium is likely to be condensed somewhat in combination, and that, consequently, the smallest number 0·711 is likely to be nearest to the truth. But the mean of the two extreme numbers will probably be admitted as a more legitimate deduction from the experiments on the compound alloys, and 0·733 be accepted provisionally as the approximate density of hydrogenium.

Could the density of hydrogenium be more exactly determined, it would be interesting to compare its atomic volume with those of other metals; and even with the imperfect information we possess, one or two points may be worthy of notice. Palladium is 16·78 or 17·3 times denser than hydrogenium, accordingly as the density of the latter is taken at 0·733, or at 0·711. Hence, as the atomic weight of palladium is 106·5, its atomic volume is 6·342 times greater than that of hydrogenium having the density first mentioned, and 6·156 times greater with the second density. To make the atomic volume of palladium exactly six times that of hydrogenium, the latter element should have the density 0·693.

Taking the density of hydrogenium at 7, and its atomic weight = 1, the following results may be deduced by calculation. The atomic volume of lithium is 0·826, or less even than that of hydrogenium (1). The atomic volume of iron is 5·026,

of magnesium 4·827, of copper 4·976, of manganese 4·81, and of nickel 4·67. These five metals have atomic volumes nearly five times that of hydrogenium. Palladium has already appeared to be nearly six times. The atomic volume of aluminium on the same scale is 7·39, of sodium 10·56, and of potassium 31·63.

2. *Tenacity.*

A new palladium wire, similar to that used in the experiment described on page 420, of which 100 mm. weighed 0·1987 grammes, was broken, in experiments made upon two different portions of it, by a load 10 and of 10·17 kilogrammes. Two other portions of the same wire, fully charged with hydrogen, were broken by 8·18, and by 8·27 kilogrammes. Hence we have—

Tenacity of palladium wire.....	100
Tenacity of palladium and hydrogen.....	81·29

The tenacity of the palladium is reduced by the addition of hydrogen, but not to any great extent. It is a question whether the degree of tenacity that still remains is reconcilable with any other view than that the second element present possesses of itself a degree of tenacity such as is only found in metals.

3. *Electrical Conductivity.*

Mr. Becker, who is familiar with the practice of testing the capacity of wires for conducting electricity, submitted a palladium wire, before and after charging with hydrogen, to trial, in comparison with a wire of German silver of equal diameter and length, at 10·5°. The conducting-power of the several wires was found as follows, being referred to pure copper as 100:—

Pure copper	100
Palladium	8·10
Alloy of 80 copper + 20 nickel.....	6·63
Palladium + hydrogen	5·99

A reduced conducting power is generally observed in alloys, and the charged palladium wire falls 25 per cent. But the conducting power remains still considerable, and the result may be construed to favour the metallic character of the second constituent of the wire. Dr. Matthiessen confirms these results.

4. *Magnetism.*

It is given by Faraday, as the result of all his experiments, that palladium is "feebly but truly magnetic;" and this element he placed at the head of what are now called the paramagnetic metals. But the feeble magnetism of palladium did not extend to its salts. In repeating such experiments, a horseshoe electro-magnet of soft iron, about 15 centimetres (6 inches) in height, was made use of. It was capable of supporting 60 kilogs., when excited by four large Bunsen's cells. This is an induced magnet of very moderate power. The instrument was placed with its poles directed upwards; and each of these was provided with a small square block of soft iron, terminating laterally in a point, like a small anvil. The palladium under examination was suspended between these points in a stirrup of paper attached to three fibres of cocoon silk, 3 decimetres in length, and the whole was covered by a bell glass. A filament of glass was attached to the paper, and moved as an index on a circle of paper, on the glass shade divided into degrees. The metal, which was an oblong fragment of electro-deposited palladium, about 8 mm. in length and 3 mm. in width, being at rest in an equatorial position—that is, with its ends averted from the poles of the electro-magnet—the magnet was then charged by connecting it with the electrical battery. The palladium was deflected slightly from the equatorial line by 10° only, the magnetism acting against the torsion of the silk suspending thread. The same palladium, charged with 604.6 volumes of hydrogen, was deflected by the electro-magnet through 48° , when it set itself at rest. The gas being afterwards extracted, and the palladium again placed equatorially between the poles, it was not deflected in the least perceptible degree. The addition of hydrogen adds manifestly, therefore, to the small natural magnetism of the palladium. To have some terms of comparison, the same little mass of electro-deposited palladium was steeped in a solution of nickel of sp. gr. 1.082, which is known to be magnetic. The deflection under the magnet was now 35° , or less than with hydrogen. The same palladium being afterwards washed and impregnated with a solution of protosulphate of iron of sp. gr. 1.048, of which the metallic mass held 2.3 per cent. of its weight, the palladium gave a deflection of 50° , or nearly the same as

with hydrogen. With a stronger solution of the same salt, of sp. gr. 1.17, the deflection was 90° , and the palladium pointed axially.

Palladium in the form of wire or foil gave no deflection when placed in the same apparatus, of which the moderate sensitiveness was rather an advantage in present circumstances; but when afterwards charged with hydrogen, the palladium uniformly gave a sensible deflection of about 20° . A previous washing of the wire or foil with hydrochloric acid, to remove any possible traces of iron, did not modify this result. Palladium reduced from the cyanide, and also precipitated by hypophosphorous acid, when placed in a small glass tube, was found to be not sensibly magnetic by our test; but it always acquired a sensible magnetism when charged with hydrogen.

It appears to follow that hydrogenium is magnetic, a property which is confined to metals and their compounds. This magnetism is not perceptible in hydrogen gas, which was placed both by Faraday and by M. E. Becquerel at the bottom of the list of diamagnetic substances. This gas is allowed to be upon the turning point between the paramagnetic and diamagnetic classes. But magnetism is so liable to extinction under the influence of heat, that the magnetism of a metal may very possibly disappear entirely when it is fused or vaporized, as appears with hydrogen in the form of gas. As palladium stands high in the series of the paramagnetic metals, hydrogenium must be allowed to rise out of that class, and to take place in the strictly magnetic group, with iron, nickel, cobalt, chromium, and manganese.

5. *Palladium with Hydrogen at a High Temperature.*

The ready permeability of heated palladium by hydrogen gas would imply the retention of the latter element by the metal even at a bright red heat. The hydrogenium must, in fact, travel through the palladium by cementation, a molecular process which requires time. The first attempts to arrest hydrogen in its passage through the red-hot metal were made by transmitting hydrogen gas through a metal tube of palladium with a vacuum outside, rapidly followed by a stream of carbonic acid, in which the metal was allowed to cool. When the metal was afterwards examined in the usual way, no hydrogen could be found

in it. The short period of exposure to the carbonic acid seems to have been sufficient to dissipate the gas. But on heating palladium foil red-hot in a flame of hydrogen gas, and suddenly cooling the metal in water, a small portion of hydrogen was found locked up in the metal. A volume of metal amounting to 0.062 c.c. gave 0.080 c.c. of hydrogen; or, the gas, measured cold, was 1.306 times the bulk of the metal. This measure of gas would amount to three or four times the volume of the metal at a red heat. Platinum treated in the same way appeared also to yield hydrogen, although the quantity was too small to be much relied upon, amounting only to 0.06 volume of the metal. The permeation of these metals by hydrogen appears, therefore, to depend on absorption, and not to require the assumption of anything like porosity in their structure.

The highest velocity of permeation observed was in the experiment where four litres of hydrogen (3,992 c.c.) per minute passed through a plate of palladium 1 mm. in thickness, and calculated for a square metre in surface, at a bright red heat a little short of the melting-point of gold. This is a travelling movement of hydrogen through the substance of the metal with the velocity of 4 mm. per minute.

6. *Chemical Properties.*

The chemical properties of hydrogenium also distinguish it from ordinary hydrogen. The palladium alloy precipitates mercury and calomel from a solution of the chloride of mercury, without any disengagement of hydrogen; that is, hydrogenium decomposes chloride of mercury, while hydrogen does not. This explains why M. Stanislas Meunier failed in discovering the occluded hydrogen of meteoric iron, by dissolving the latter in a solution of chloride of mercury: for the hydrogen would be consumed, like the iron itself, in precipitating mercury. Hydrogen (associated with palladium) unites with chlorine and iodine in the dark, reduces a persalt of iron to the state of protosalt, converts red prussiate of potash into yellow prussiate, and has considerable deoxidising powers. It appears to be the active form of hydrogen, as ozone is of oxygen.

Discussion on Dr. Williamson's Lecture on The Atomic Theory,
November 4th, 1869.

Sir BENJAMIN C. BRODIE, Bart., F.R.S., in the Chair.

THE Chairman said the business before the Society was to consider a paper "On the Atomic Theory," which had already been read before the Society by Professor Williamson. This theory was not to be regarded as a fixed and definite system of ideas, but one that had undergone great variation and change. There was the atomic theory of Dalton; then that of Berzelius, and also, that of Laurent and Gerhardt; and now they had come to a further form of this theory, in which new ideas had arisen in regard to the nature of atoms and their properties; and he (the Chairman) thought it would greatly facilitate the discussion if Dr. Williamson would explain what was the precise form of the atomic theory which he was prepared to maintain and defend, and how they might discriminate that from other forms of the theory, some of which Dr. Williamson himself would admit to be neither reasonable nor rational. First, there was the question whether there were atoms at all; then, being atoms, what those atoms were, and whether they were endowed with the properties assigned to them in regard to their replacing power, and to what was termed their value. These were the questions raised by the lecture of Dr. Williamson, and which they were now to discuss.

Professor Williamson said that he did not admit that, among chemists, there had been several atomic theories. If there had been, he had yet to learn of them. There had prevailed, he believed, from time immemorial, a belief that matter was built up of small particles; and he might also say that no contrary opinion had ever been embodied in any definite form. Dalton doubtless looked for evidences of what he believed to be true, and saw, in the simple multiple proportions which he specially alluded to, facts which were in accordance with that preconceived conviction; but his was the mere germ of an atomic theory, and the changes which have taken place in it since are consistent with the original notions. The very rapid changes had, in the main, been additions to the starting-point given by Dalton. The line of work so vigorously pursued of late years by many chemists, regarding the order in

which atoms are arranged in their compounds, was mentioned by the speaker. His endeavour had been to put together more fully than had been done of late, what is known of the chemical evidence: firstly, respecting the limits to the divisibility of matter, and, secondly, with regard to the properties of those finite particles which constitute the limits of divisibility, solely from the point of view habitually employed by chemists in their ordinary working. He had also endeavoured to separate those conclusions which appeared to him warranted by facts from everything else. Whether the smallest particles of matter have a spherical form or not, whether they are in their nature indivisible, whether they are in reality the ultimate atoms of matter, or like the planets of this system, he knew not, nor did such questions exist for him as a chemist. He therefore thought it wise to exclude them, important as they were, from the actually existing atomic theory. The work of Berzelius was perhaps the most significant transition from the original notion of Dalton. Silently these atoms had been accepted by chemists, and the whole course of investigation had been one grand confirmation of the assumption, that compounds must have molecular weights corresponding to at least the smallest atomic proportion which would represent the actual numbers of analysis. The perfectly independent observations which had been made with reference to the boiling points of homologous liquids, the phenomena of diffusion, and the equality of volumes of masses containing an equal number of these molecules under similar conditions in the gaseous state: all concurred to corroborate the conclusions necessitated by the atomic theory. Thus, independent workmen hewed stones which, when hewn, were found to fit in exactly with the others, forming a perfectly homogeneous whole. Dr. Williamson concluded his remarks by referring to the atomic values, a term which, he thought, represented in a more precise way than some others what is called atomicity; and he also referred to the difference between direct and indirect combination, a fact which he conceived to be essentially atomic in its nature.

Dr. Frankland said that he was not present when Professor Williamson delivered his lecture, and he had only cursorily looked over the printed report; but, so far as he could gather, the object of the author had been to establish the atomic theory as an absolute truth. There had been, he thought, so little, if any

opposition to the application of the atomic theory to the phenomena of chemistry, that a discussion could scarcely be raised upon any other feature of the question than that of its absoluteness. He considered it impossible to get at the truth, as to whether matter was composed of small and indivisible particles, or whether it was continuous—the question belonged to what metaphysicians termed “the unknowable;” but he acknowledged the importance of the fullest use of the theory as a kind of ladder to assist the chemist in progressing from one position to another in his science. He was, however, averse to accepting the theory as an absolute truth. Any attempt to realise by its help the action of attractive or repulsive forces upon matter was excessively difficult; indeed to realise such an action through a perfectly void space was to him quite impossible. The same difficulty presented itself to Faraday, who was often obliged to throw this atomic theory on one side, as an obstacle to his progress. He said that if matter be assumed to be thus composed of solid particles separated by a void space, then, in considering the phenomena of electricity in connection with that view of matter, this space existing between the atoms must be either a conductor or a non-conductor of electricity. If a conductor, such a thing as an insulator was obviously an impossibility; if it was a non-conductor, such a thing as a conductor was equally inconceivable; so that, apart from chemistry, there were considerations which made it very undesirable that this theory should be represented as an absolute truth. The speaker then referred to the combination which, in certain cases, is effected between gases by the application of heat, and said that, according to the atomic hypothesis, they must assume that the gases, when heated, have their particles driven further asunder; but how, then, could they more readily enter into combination when heated, as in the case of oxygen and hydrogen, and in many other similar instances? No such difficulty presented itself if the gases were regarded as continuous matter. He admired the atomic theory as much as Professor Williamson, and he thought no one could blame him for not making a sufficient use of it; but he did not wish to be considered a blind believer in the theory, or as unwilling to renounce it if anything better presented itself to assist him in his work.

Dr. Odling said that, as a chemist, he was not particularly interested in the question whether matter is infinitely divisible

or not, but he did not think that Dr. Williamson's argument had established that conclusion. Dalton was always spoken of as the discoverer of the law, or doctrine, or theory of combination in definite and multiple proportions, to account for which his invention or adoption of the atomic theory was founded; but he conceived that Dalton's great discovery might be better expressed as the law of combination in *reciprocal* and multiple, instead of in *definite* and multiple, proportions. Dalton, in fact, discovered that, if we have three different kinds of matter, A, B, and C, and we find that x times A unites with y times B, and with z times C, then if B and C can combine with one another, it is in the proportion of y and z , or some simple multiples thereof. These were the great facts which Dalton discovered; he showed that they were applicable to all the cases known in his day, and they have proved applicable to all the cases that have been discovered since. Dr. Williamson had said of chemists, that all their modes of thought, and all the government of their actions, are based upon the atomic theory; be he (Dr. Odling) maintained that they are based upon the observed fact that certain bodies combine in certain proportions. Dr. Williamson also argued that the atomic theory is based upon the existence of molecules, and that molecules have no *locus standi* in the absence of the atomic theory. He (Dr. Odling) disputed that position; for the fact that the hydrogen existing in marsh-gas is divisible into four parts, and the hydrogen existing in ammonia only into three parts, is, he conceived, a fact quite independent of the atomic theory. The laws of combination, as far as they go, were compared by Sir Humphry Davy to Kepler's laws of planetary motion, which were simply a general expression of observed facts; and, in the same way, these laws of chemical combination are general expressions of observed facts upon which the atomic hypothesis is superinduced.

Professor Miller thought that Dr. Odling's arguments had not disproved the atomic theory. If we have not the atomic hypothesis, it may fairly be asked what explanation we possess of the laws of combination? Certain facts are admitted on all hands, as determined by experiment, and when an important and extensive series of facts has been ascertained, the endeavour to explain them by some supposition which embraces the facts, and enables us to anticipate new ones if possible, is a necessary

result of our mental constitution. Unless some hypothesis is accepted, it is absolutely impossible to reason upon the facts; and, even if we cannot adopt this hypothesis as absolutely true, such a view of the constitution of matter at least explains all the chemical facts that have hitherto been presented. It appeared to him that those who deny the atomic hypothesis are bound to supply something to enable them to interpret phenomena with the same regularity and order as that hypothesis, the accuracy of which they deny and which they desire to displace. No one would suppose that the absence of an undulatory theory for light would conduce to the explanation of optical science; and he held that what the undulatory theory is to the phenomena of light, the atomic theory is to the phenomena of chemistry.

Professor Foster thought the question before the Society was not so much the utility of the atomic theory as its truth. To say that the atomic theory has been very useful, and that, if we refuse to admit it, we have nothing to put in its place, is not exactly the point. A false theory may for the time be an exceedingly useful one, but the present question is whether the atomic theory is true or false, not whether it is a useful or useless theory. With the notions which we are in the habit of entertaining as to the nature of combination, we can indeed scarcely avoid the atomic theory. Naumann has stated, in his "Relations of Heat to Chemistry," that, if we assume that in any compound body the components really occupy distinct portions of space, we must assume that body to be incapable of infinite divisibility. To take a concrete case, he speaks of vermilion. Assuming that in this body the sulphur and mercury occupy separate portions of space, and do not interpenetrate, then we know that so far as any actual division goes, we can separate the portion of vermilion into smaller and smaller bits, but each bit is in itself still a perfect bit of vermilion, containing sulphur and mercury. If, however, we could carry the division further, we must ultimately come to the point at which any further division would give us dissimilar portions of matter, at which, indeed, we should actually have broken off the sulphur from the mercury, and thus have arrived at an atom of this compound body vermilion. He (Professor Foster) thought, however, that the ideas generally entertained of the existence of the constituents of bodies in compounds are not absolutely necessary ideas.

The fundamental phenomenon of every chemical change may perhaps be stated in some such terms as these. We begin with some kind or kinds of matter, say oxygen and hydrogen; we perform a certain operation; these kinds of matter disappear, and another kind of matter, viz., water, begins to exist. But it is, perhaps, after all, a conventional mode of expressing the fact, to say that the oxygen and hydrogen are contained in the water. We know that between the bodies which disappear and the body which appears, there are certain relations, not only qualitative but quantitative, the total mass of the disappearing substances being equal to that of the appearing substances; but we may perhaps return, sometimes, at any rate, with great benefit, to the notion that one portion of matter is actually transmuted into another; that it ceases to exist as such, but something else comes in place of it. From such ideas the existence of atoms would not follow as a necessity, but with our present mode of stating and reasoning about chemical changes, an atomic hypothesis or basis appears to be inevitable.

Professor Tyndall sympathized with the ideas of Professor Williamson; his thoughts had, to some extent, been expressed by Dr. Miller, who had made a strong point in referring to the undulatory theory. It would be quite possible, to detach the phenomena of light from the physical theory of an ether; to say, indeed, that the undulatory theory is something superinduced upon the facts, and a mere imagination. "Still," said Dr. Tyndall, "I do not think we should suffer ourselves to be fettered in that way, and I did certainly expect that Dr. Odling would have gone one step further when he referred to Davy's allusion to the laws of Kepler. Those laws stated the facts of planetary motion as clearly as we know them at the present time; but facts are not sufficient to satisfy the human mind. Another man followed Kepler, and superinduced something upon the facts—a something which we now know as the theory of gravitation. I say it is the nature of the human mind, whenever it attains to any degree of depth—it is the nature of a profound thinker when he ponders upon phenomena of this nature, to seek for some underlying principle—something altogether outside the region of facts—from which he deduces the facts as consequences. Professor Foster has very justly remarked that the usefulness of a theory is not a justification for holding what Professor Frankland has called an absolute

truth, and that a bad theory is very often useful. Undoubtedly it is. The emission theory of light was useful in the hands of Newton, Malus, Laplace, and especially of Brewster; and still the emission theory fell. Why did it fall? Because in the progress of investigation phenomena were observed which were perfectly inexplicable upon the emission theory, but which have been completely explained by the undulatory theory. The undulatory theory will stand in front of all opposition as long as it is competent to explain the facts of optics; and I apprehend that the atomic theory will stand as long as it is competent to explain the facts of chemistry."

Dr. Mills observed that to prove the truth of the atomic theory, one of the most important points to establish would be that the general analogy of nature is in favour of indivisibles, whereas the very contrary is the fact. The great kingdoms of nature, animal, vegetable, and mineral, have no positive lines, but pass into one another by imperceptible gradations, as likewise do the forms of nature, geographical, physiological, and crystallographical. In comparing the atomic theory with the undulatory theory of light, it should be remembered that the latter has this advantage, that we have often seen the phenomena of waves, and therefore if an ether exists, it may have a wave-like motion. The existence of waves is a fact; but the existence of atoms, or, in short, of a limit of any sort in nature, is not a fact. No one has ever seen an atom, and in this respect the atomic theory has an exact parallel in the theory of phlogiston. Dr. Mills further remarked that it seems to be forgotten by many writers that matter might be infinitely divisible, and yet that definite proportions might exist; for between two infinities there may be a finite ratio, so that the atomic theory is not perfectly necessary to chemistry. He believed that motion is the highest generalization of modern science, and it therefore affords the only criterion by which all theories, including those of chemistry, must be judged, and the notion of a limit is practically inconsistent with the idea of motion.

Dr. Williamson, in his reply, remarked that the benefit accruing from looking at the question from another point or view would be incalculable, and if another view were developed to supersede the present one, he would be among the first to rejoice at it, but he had not to do with the future of this

matter. He had endeavoured to put together the actual evidence of the present view, and none of its opponents had been able to find a fallacy in that evidence. He thought it most important to keep the theory, at each period of its growth, in the modest position which it at present occupies, that of generalizing the best ascertained relations of the elements in their chemical changes.

The Chairman said that he liked to have clear and definite ideas, as far he was able to realize them, on scientific subjects, and he was unable to consider even an atomic theory in the abstract. The atomic theory, as he understood it, was—that any given portion of matter is made up of a number of finite particles, the aggregate of which could be divided and subdivided until at last only one indivisible particle would remain, and this view might be derived from the perusal and common assent of every work on chemistry that defined the atomic theory. He thought that such a view as the physical indivisibility of matter must be separated from the facts and basis of chemistry. Dr. Williamson seemed to think the theory and facts were one, but he (the Chairman) asserted that they are two distinct things. He must also express his dissent from the views expressed by Drs. Frankland and Miller, with reference to the use of a doctrine or theory in which they do not believe. He could not understand using a theory and denying it at the same time. This theory had, he thought, been often the means of deluding chemists into the belief that they understood things about which they knew nothing. He found the works of Kekulé and Naquet scribbled over with pictures of molecules and atoms, arranged in all imaginable ways, for which no adequate reason was given, and if there was no reason for this, it was a mischievous thing to do, for it led to a confusion of ideas, and to mixing up fictions with facts. Many students, he believed, thought the atomic pictures in Naquet's work were the fundamental things to be studied in chemistry; they did not draw the distinction between the facts and theory of the science. His view was that the ultimate constitution of this material universe was one of those questions upon which no light had yet been thrown, and he agreed with Dr. Odling when he said that the science of chemistry did not require or prove the atomic theory. Chemists were bound to have some real and adequate means of working at the science of

chemistry, and discovering its laws, and they could effect this, either through the investigation of the laws of gaseous combination, or the study of the capacity of bodies for heat. When they approached the science through the study of gaseous combinations, they discovered that the combining proportions of bodies are capable of being represented by integral numbers, and they also found an analogous fact in studying the capacity of bodies for heat. Either of these methods might be made the basis of the science, and lead to the same general system of ideas, in which we retain what is valuable in the atomic theory, without committing ourselves to a number of assertions incapable of proof.

XXXVII.—*On the Formation of Carbonic Ether.*

By WM. DITTMAR, F.R.S.E., and GEO. CRANSTON, Edinburgh.

(Read Nov. 18th, 1869.)

WHEN oxalate of ethyl is heated with sodium or potassium, the metal dissolves, with evolution of a large quantity of carbonic oxide; and there is produced a dark-coloured mass, which, on distillation yields a liquid consisting, substantially, of carbonate of ethyl mixed with more or less undecomposed oxalate. This reaction, as is well known, was discovered many years ago by Ettling,* but has not yet found a satisfactory explanation based on experiment. In order to find out, if possible, the *rationale* of the process, we made a number of experiments, of which the following is a short account.

Starting with the assumption that the first step in the action of the potassium or sodium on oxalate of ethyl was the decomposition of some of the latter into carbonic oxide and potassium ethylate (EKO); we tried the action on oxalate of ethyl, of ready-formed sodium ethylate (ENaO), and soon found that this compound, like the metal itself, causes the formation of carbonic ether and carbonic oxide. If, for this purpose, ordinary so-called alcoholate (*i.e.*, the liquid obtained by dissolving sodium in perfectly anhydrous ethylic alcohol) be used, a considerable quantity of carbonic oxide is evolved; but the yield of carbonate of ethyl is very small, a great pro-

* *Annalen der Chemie und Pharmacie*, xix, 17.

portion of the oxalate, as well as of the temporarily formed carbonate, being changed into ordinary ether (E_2O), and sodium oxalate, and carbonate. A much better result is obtained, and the reaction goes on far more regularly, if the real compound $ENaO$ be used. Dry ethylate, $ENaO$, we easily succeeded in preparing, by evaporating the liquid alcoholate (prepared from alcohol previously dehydrated by distillation over sodium, in a current of dry hydrogen, within a retort heated in an oil-bath) when the compound remained as a white porous mass, which, in an atmosphere of hydrogen, can be kept for a long time at 180° — 200° C without suffering apparent decomposition.* When dry ethylate of sodium is brought together with a large excess (eight times its weight, or more) of oxalic ether in the cold, it gradually dissolves, with slight evolution of heat and formation of a yellowish syrup, which sometimes gelatinizes on standing. Most probably a molecular compound of oxalate of ethyl and ethylate of sodium is produced, which, however, we did not succeed in obtaining in a definite shape. If this mixture is heated gradually—best by means of an oil-bath—a strong reaction is observed to set in at about 80° C.; large quantities of a gas (substantially carbonic oxide) are evolved, and the mass becomes darker and darker in colour—at last almost black. By gradually raising the temperature to about 140° the reaction is soon brought to a close. If the resulting mass is now distilled—we always carried out the distillation in a current of hydrogen, heating the retort in an oil-bath kept at temperature not exceeding 200° —there is obtained a *distillate* consisting of carbonate of ethyl mixed (or not, according to the relative proportions of materials used), with undecomposed oxalate, and invariably containing also a small quantity of ethylic alcohol, even if the most carefully dehydrated and dealcoholated substances were used.

* We are here bound to state, however, that in all our syntheses of $ENaO$, the weight of the compound, after complete desiccation at 180° C. (in dry hydrogen), was invariably short of that calculated from the weight of metal used, by from 3 to 6 per cent. of the calculated ethylate. In one of the experiments, for instance, in which alcohol freshly distilled off sodium, and perfectly bright sodium were used, 1.788 grms. of sodium gave 5.107 grms. of ethylate, *i.e.*, 23 of Na gave 65.7 instead of 68 parts of $ENaO$. A titration of the substance with standard sulphuric acid led to the value 66.6. Some chemists say that alcohol cannot be completely dehydrated by means of sodium; if this be true, a part of the loss may have been owing to the formation of caustic soda.

The residue is black; it completely dissolves in water without evolution of a gas. The solution, on distillation, yields, substantially, pure water; more especially, no alcohol. The residue contains oxalate of sodium, a small quantity of formate, and besides these, the sodium salts of a complex of organic acids (Lowig's "nigric acid," *inter alia*), which we made many attempts to separate and define, but without success. There is not any carbonate produced; homologues of formic acid were specially searched for, but could not be detected. We never observed the formation of more than traces of ether; noteworthy quantities of the latter are formed only if the proportion of ethylate used is greater than the one above given; or if the mixture of ethylate and oxalate is rapidly heated before the ethylate is completely dissolved, by the local action of an excess of ethylate on the oxalate.

In order to obtain a basis for speculation on the nature of the reaction, we determined, in a series of experiments, made with varying proportions of carefully purified materials, the ratios to one another of the quantities of oxalate of ethyl and ethylate of sodium used, and of carbonic oxide, carbonate of ethyl, and alcohol produced. The purity of the oxalate was proved by titration. The ethylate, as a rule, was prepared *ex tempore* from a weighed quantity of sodium, and was dried in hydrogen at 180° — 200° , until it ceased to lose weight. In all these quantitative experiments, the quantity of oxalate used was at least 4 " $(\text{EO})_2\text{C}_2\text{O}_2$ " for 1 "E NaO ." The reactions were carried out, at the lowest possible temperature, in a distillation apparatus, the atmosphere of which communicated directly with that of a glass gasometer, continuously kept at a pressure equal to that of the atmosphere. The volume of gas evolved was determined by observing the expansion sustained by the atmosphere of the apparatus, and the observed volume, after applying the necessary corrections for temperature, pressure, and tension of water, reduced to weight. In one of these experiments, the gas was analyzed quantitatively, by passing a part of it (about four litres, four-fifths of the whole quantity); 1stly, through a U-tube containing pumice-stone and sulphuric acid, to absorb water, ether, and alcohol; 2ndly, through a weighed tube containing granulated soda-lime, and, at the exit end, chloride of calcium, to absorb carbonic acid; 3rdly, through a combustion tube filled with red-hot oxide of copper; and

4thly (the products of combustion), through a series of weighed absorption apparatus charged with sulphuric acid, potash, and soda-lime respectively, to absorb and determine the water and carbonic acid formed. Calculating the water formed for free hydrogen, the gas was found to contain in 100 parts by weight,

Hydrogen	0.1
Carbonic acid	0.4
Carbonic oxide.....	99.5

The ethereal distillate was weighed, and, at least qualitatively, tested for oxalate. In some cases, the proportion in it of carbonate of ethyl was determined by decomposing a weighed portion in a closed vessel with pure caustic soda, decomposing the carbonate of sodium formed with hydrochloric or sulphuric acid, and collecting the carbonic acid liberated (after previous absorption of water and alcohol by sulphuric acid), the bulk in solution of potash, the rest in granulated soda-lime. The quantity of oxalate of ethyl decomposable by a given weight of ethylate of sodium was found out by tentative experiments, *i.e.*, by adding to a weighed quantity of oxalate small successive quantities of ethylate, and, after each addition, heating as long as any more gas was evolved.

The successive volumes of carbonic oxide evolved (and probably also the quantities of carbonate of ethyl formed) were found to be proportional to the corresponding weights of ethylate of sodium added. Allowing the several experiments to mutually supplement each other, we were led to the following conclusions:—

“E₂NaO” parts of ethylate, acting upon an excess of oxalic ether, decompose 4“(EO)₂C₂O₂” parts of oxalate of ethyl, and produce 3“(EO)₂CO” parts of carbonate of ethyl, 3“CO” parts of carbonic oxide, and about 0.4 “EHO” parts of alcohol. Each of the ratios here given is the result of a number of experiments, in which the direct experimental numbers came as near the integers here adopted as could be expected in experiments of this nature.

The experiments adduced up to this point were carried out in the University Laboratory, Edinburgh, during the winter session of 1867-68.* One of us has lately supplemented them (in

* At the Norwich meeting of the British Association (1868), the before-mentioned results were communicated, privately, to a number of chemists, among them to

Prof. Kekulé's Laboratory at Bonn) with a few experiments on potassium ethylate.

Dry ethylate of potassium is easily prepared in the same way as the sodium compound. The liquid alcoholate, when evaporated, in a current of dry hydrogen, in a retort heated by means of an oil-bath, leaves an oil, which, on continued exposure to 150° — 180° C., slowly gives up the last traces of alcohol, and leaves the compound EKO as a white mass. This body, in an atmosphere of dry hydrogen, stands a temperature of 200° without observable change. Its behaviour to oxalate of ethyl, qualitatively, is quite analogous to that of sodium ethylate, only the reaction is more energetic and commences at a lower temperature. But the quantity of oxalic ether decomposed, per atom of metal, was found to be far more considerable. A quantitative experiment gave the following numbers:—

$1 \times "EKO"$ (direct observation, $1.02 \times K + 0.98 \times EO$) in acting upon 12.9 " $(EO)_2C_2O_2$ " gave 6.7 " CO ", and a distillate containing 6.2 " $(EO)_2CO$ ", 4.5 " $(EO)_2C_2O_2$ " and about 1.6 " EHO ".

Taking all our results together, and considering especially that carbonic oxide and carbonate of ethyl were always produced in very nearly equal numbers of molecules, as if the greater part of the oxalate of ethyl had simply been split up into these two compounds, and that (in the case of potassium ethylate) the quantity of oxalate thus decomposed, per molecule of EKO used, amounted to upwards of six molecules, it is scarcely possible to evade the conclusion that, in the process considered, we have to deal with a catalytic reaction; *i.e.*, a cycle of reactions in which the ethylate is continuously decomposed and reproduced; and that a given weight of potassium ethylate could decompose unlimited quantities of oxalate of ethyl, if it were possible to exclude certain other reactions, which go on side by side of the main one, and gradually consume the ethylate. Whether or not these other reactions are an essential condition for the main reaction setting in at all, can, of course, be decided only by further experiments.

Professor Wanklyn said that in 1864 he had read a paper to the Society on "The Constitution of the Fatty Acids," wherein

Mr. Wanklyn. Compare the publications of that gentleman in *Chemical News*, 25th September, 1868; and *Phil. Mag.* (Memoir on Ethylate of Sodium).

he regarded the ethers as compounds in which the acid-forming radical is the metal, and the ethyl-oxide the chlorous radical. He also presented a paper on the reaction treated of by the authors, and predicted that ethylate of sodium would decompose oxalic ether, producing carbonic oxide and a carbonic ether, and that an unlimited quantity of oxalic ether might be decomposed by a given quantity of ethylate of sodium; but that paper was not published by the Society. It was gratifying to him to find his prediction verified so long afterwards by gentlemen who had made the experiment, without any communication with, and quite independently of, himself.

XXXVIII.—*On the Dissociation of Liquid Sulphuric Acid.*

By WM. DITTMAR, F.R.S.E.

It was shown by Marignac,* in 1853, that hydrated sulphuric acid, of any strength, ($\text{H}_2\text{SO}_4 + x\text{H}_2\text{O}$ as well as $\text{H}_2\text{SO}_4 + x\text{SO}_3$) when boiled down, until the composition of the residue no longer changes, leaves, not as was generally supposed at the time, pure monohydrate, H_2OSO_3 , but a liquid of the composition $\text{SO}_3 + 1\frac{1}{2}\text{H}_2\text{O}$. According to Marignac, the only qualitative method for preparing the substance H_2SO_4 is to expose an oil of vitriol, possessing as nearly as possible this composition—for instance, the acid stable on boiling—to a very low temperature, when the real compound H_2SO_4 separates out as crystals, the small excess of H_2O or SO_3 remaining in the mother liquor. The crystals melt at $10^\circ.5$ C.; the liquid, when heated to about 30° — 40° gives off vapours of anhydride, and when boiled down is soon reduced to $\text{SO}_3.1\frac{1}{2}\text{H}_2\text{O}$. These observations of Marignac's seem to show that " H_2SO_4 ", in spite of the great amount of energy liberated in the union of its components H_2O and SO_3 , exists as a definite chemical individual only in the solid state, and that liquid H_2SO_4 , even at low temperatures, must be looked upon as a molecular mixture. Which chemical individuals must be assumed to be

* *Archive des Sciences Physiques, etc.*, Genève, xxii, 225; *Jahresbericht* for 1853, page 324.

present in this mixture? It seemed to me that probably a step towards the solution of this problem might be made by investigating the behaviour of the acid H_2SO_4 when boiled under pressures differing considerably from that of the atmosphere. I have therefore made a series of experiments in this direction.

A considerable quantity of pure distilled oil of vitriol was mixed with anhydride so as to bring up its strength to about 99.5 per cent. (of H_2SO_4). This acid was used in all distillations. The apparatus consisted, essentially, of a retort, just large enough to accommodate all the boiling fluid, connected hermetically with a receiver, which, in its turn, by a branch soldered on to the bulb, communicated with an air-pump (constructed so as to serve for rarefying as well as condensing) or mercury manometer, and, in order to avoid sudden changes of pressure, with an "artificial atmosphere" of about five litres. In each experiment about 100 grms. of acid were used.

The desired pressure having been established, the liquid was heated up to, and maintained in, rapid ebullition until about one-half of it had distilled over. In the distillation at *pressures less than one atmosphere*—to avoid the otherwise extremely violent bumping—it was found necessary to pass a current of air through the boiling acid. For this purpose the retort was provided with a narrow thermometer-tube, soldered on to the lowest point of the bulb, and bent upwards; and through this tube a properly regulated slow current of air, previously dehydrated by means of sulphuric acid, was allowed to pass into the boiling liquid. The volume of air required for producing a regular ebullition was very small, so as scarcely to affect the manometer—an occasional pull at the air pump maintaining it sufficiently constant. The retort was heated within a double air-bath; two mica plates, inserted at the proper places, admitted of the process being watched. In the experiments at *pressures greater than one atmosphere* the current of air was found unnecessary, and was therefore dispensed with. Oil of vitriol when distilled under pressure boils regularly, the more so the greater the pressure; under an extra pressure of about two atmospheres, as regularly as water containing dissolved air. In the distillation-apparatus used for these experiments, the retort and receiver were in one piece (of the shape of a cryophorus) a branch tube soldered on to the receiver bulb

serving to introduce the acid, and, subsequently, to attach the manometric apparatus. The retort-bulb, after having been charged with acid, was placed in a sand-bath between two hemispherical iron basins, fitting rim to rim, and held together by means of two rings of a retort stand. The manometric apparatus was then attached, the proper pressure established, and about one-half of the acid driven over by a rapid distillation.

As soon as a distillation was finished, the apparatus was cooled down as quickly as possible, the retort detached from the receiver, a part of the residue (about 10—20 grms.) weighed out in a flask provided with a glass cap, diluted, with the proper precautions, with water to exactly ten times its weight, and the dilute liquid preserved for analysis. All of the dilute liquids were subsequently analyzed, by titration, with the *same* standard solution of caustic soda. In some cases, the percentage of acid in the liquid was determined with a higher degree of precision, by adding to a weighed quantity (4 to 5 grms.) of pure carbonate of sodium a slight excess of the dilute acid, boiling off the carbonic acid, and then titrating back with standard caustic soda. The results are given in the following table, in which P stands for the pressure (in ctm. of mercury) under which the distillation took place. Equivalent means the equivalent of the acid obtained as a *residue*, i.e., the quantity requiring for saturation 23 parts of sodium,

No. of Expt.		P.	Equivalent determined with NaHo sol., dry N_2CO_3 .		
1....	5.5*(?)	49.6 } 49.4 }			
2....	2.8	—	{ 49.41 } 49.53	} Distilled in cur- rent of air.	} Marignac, distilling without a current of air, found E = 49.75.
3....	3.0	49.4	49.47		
4....	37	49.6			
5....	35	49.5			
6....	76—2 or 3 ctm.	49.6			
7....	76.6	49.6	49.70		
8....	166	—	49.88		
9....	180*(?)	—	49.78		
10....	214	—	49.82		

It is seen that in all the distillations, although they extended over a considerable range of pressures, the residues obtained were almost identical in composition with Marignac's acid. Considering, now, that the acid originally started with was

* Rough estimate, data for exact determination of P having been lost.

only little stronger than such acid (99.5 per cent. of H_2SO_4 , corresponding to the equivalent 49.25), it is fair to assume that in each distillation the point of equilibrium was passed, *i.e.*, that a further concentration of the residue would not have led to any further change in its composition. The equivalents, as the table shows, range from 49.5 as a minimum, to 49.9 as a maximum, *i.e.*, they differ from 49.7 only by amounts which are almost within the limits of the unavoidable errors of analysis. In other words, sulphuric acid, when boiled down under any pressure between 3 atm. and 314 atm., behaves almost like a mixture of the stable hydrate $12\text{SO}_3 \cdot 13\text{H}_2\text{O}$ + excess of SO_3 . To deduce from this fact the existence of a stable *molecule* of this composition would, of course, be monstrous. The observed facts can perfectly well be accounted for without denying that in liquid sulphuric acid, even at its boiling point, the majority of the molecule has the composition H_2SO_4 . We need only call to aid Clausius' theory of temperatures, which, in the hands of Naumann, Hoistmann, and others, has already thrown so much light on the dissociation of gases. We know that H_2SO_4 vapour consists chiefly, from a certain temperature upwards entirely, of isolated molecules of SO_3 and H_2O . Now, it is quite in accordance with Clausius' theory to assume that in liquid sulphuric acid, even at low temperatures, a number of the molecules have already assumed the state of motion corresponding to a temperature beyond the temperature of dissociation. The higher the temperature, the greater the ratio of the number of dissociated molecules to that of the unchanged ones. The liberated H_2O 's and SO_3 's, being formed in the midst of a mass of (H_2SO_4) 's, will probably mostly unite with comparatively cold molecules of H_2SO_4 , and form compounds $\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4 \cdot x\text{SO}_3$ respectively. Assuming, now, the latter compounds to be less stable than the former, it is easily understood that, in the distillation of sulphuric acid, SO_3 (as against $\text{SO}_3 + \text{H}_2\text{O}$) will predominate in the vapour, the more the higher the temperature, *i.e.*, the greater the pressure under which the liquid boils.

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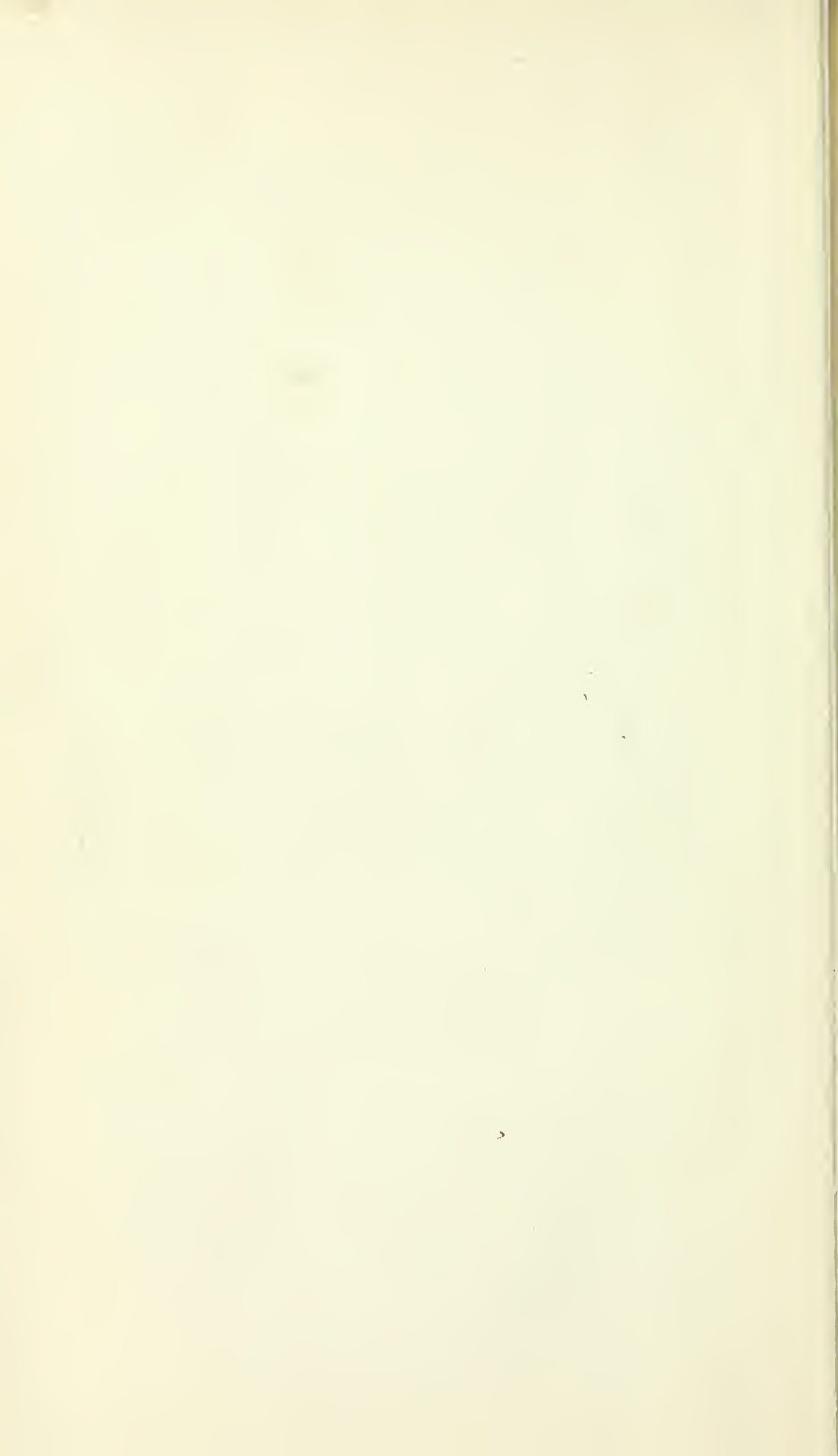
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123	{ ²¹ ₂₈ }	for	Pearson	read	Pearsall.
249	20	„	acid	„	oxide.
—	21	„	6 lbs.	„	4 lbs. worth.
—	30	„	4	„	3.
250	5, 6	„	reduced a mixture of CO and	„	increased the proportion of.
200	15		<i>dele</i> sodium.		
—	—	„	sulphuretted hydrogen	„	sulphydrate of sodium.



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